EVALUATION OF STRUVITE FROM SOURCE-SEPARATED URINE AS A PHOSPHATE FERTILIZER

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Declaration

I, Nqaba Nongqwenga, declare that:

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Professor J.C. Hughes (Supervisor)

Signed…….. Date……..

Professor P. Muchaonyerwa (Co-supervisor)

ABSTRACT

The potential shortage of phosphorus (P) fertilizer is a threat to food security and closing the nutrient loop through recycling human excreta, especially urine, has been considered, so as to mitigate this crisis. Struvite (magnesium, ammonium phosphate), a material derived from human urine, is a product which is gaining credence with regards to using urine as a P amendment since more than 90% of P in urine can be captured during struvite production. A study to evaluate the potential of struvite as a P amendment in three contrasting soils was conducted. The soils used were an A horizon of Inanda (Ia), A horizon Sepane (Se) and an E horizon of Cartref (Cf).

Phosphate adsorption properties of the soils were studied and the Freundlich model used to derive sorption parameters. From these studies, Pmax was related to the K_f parameter of the Freundlich equation. Two sets of incubation studies were then conducted. The first ran for 122 days and the second for 22 days to examine in closer detail the early stages of dissolution of the struvite as the major P release occurred during this time period of the incubation. A pot experiment was conducted in a controlled environment so as to determine the effect of P released from struvite on maize growth.

The Ia, with high content of iron and aluminum oxides, displayed high sorption and affinity for P, whereas soil texture was a principal factor in the sorption properties of the Se (clayey) and Cf (sandy). The K_f decreased in the order Ia > Se > Cf and external P requirements decreased in the order Se > Ia > Cf. In the incubation studies solution P content increased with an increase in application rate of struvite. Struvite dissolution and P release varied between the different soils and the dissolution was found to be related to the P adsorption maximum of each individual soil and soil pH. The magnesium content also increased with time.

In the glasshouse study, drymatter yield after six weeks growth was improved by the addition of struvite. There were no benefits achieved by using more than the recommended application rates for each soil. Struvite was as effective as conventional single superphosphate in the Ia and Cf, while superphosphate outperformed struvite on the Se. The findings of this study suggest that struvite has the potential to release P in an available form although its effectiveness and

capability to release P could depend on soil pH, exchangeable acidity and initial P levels. Further research needs to focus on the effect of pH on struvite dissolution, the effect of struvite on soil pH, as well as comparison of nutrient release patterns between struvite and rock phosphate.

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CHAPTER 1

INTRODUCTION

The world's main source of phosphorus (P) is phosphate rock. Although phosphate-bearing minerals appear abundant, a major portion of phosphate deposits cannot be commercially exploited using available technology (Mavinic et al., 2009). These commercial but currently non-viable deposits include resources on the continental shelves and seamounts. Phosphorus reserves are not uniformly distributed, but are concentrated in specific parts of the world with 50% of the world's reserves located in the Middle East and north Africa. The largest known deposits of apatite (the main phosphate mineral) are located in China and Morocco (Cooper et al., 2011).

There are contrasting views surrounding the future supply and demand for P. The major concern is that future supply will not be able to meet demand due to the possible exhaustion of the currently known and commercially available reserves. Food security of the world in the near future might depend on the few countries, which own the reserves and in many cases such countries are currently politically sensitive and volatile. According to Vaccari and Strigul (2011), the estimated known reserves are around 16 billion metric tons, and are being mined at a rate of 158 million metric tons per year. Thus, if these figures are correct, a complete depletion of P reserves will occur within a century. These numbers are based on data from the US Geological Survey (USGS, 2008). An assessment by Van Kauwenbergh (2010), however, suggested that there is no threat to P sources for at least the next two millennia. The potential P crisis is further exacerbated by the rapidly growing population. If population, and hence demand for food, continues to grow exponentially phosphorus requirements might triple in the next century. There is no single response available to mitigate this crisis, but rather an integration of responses might be required so as to ensure future supply.

Several strategies have been proposed so as to maintain or sustain future supplies and these include (a) preserving P by reducing soil erosion, through implementing conservation tillage practices; (b) recycling waste including human excreta and other waste materials; and (c) seeking

new sources that includes researching new ways of extracting minerals economically, so as to exploit currently non-economically viable deposits (Vaccari, 2009).

Each of these proposed solutions has limitations that vary on a country or regional basis. For example; in countries where there has been less input of P onto the land initially, as is the case with many developing countries, conservation would not be the solution to their P related problems. Not all countries have P deposits and thus researching new ways of exploiting currently non-viable deposits would not be as immediately beneficial as it would be for countries with such deposits. Waste recycling, however, is one of the more promising answers due to the ubiquitous occurrence of waste material. Waste recycling for P recovery will be able to benefit both developing and developed countries, and countries with or without phosphate rock deposits.

Nutrient extraction from waste material, including the separation and collection of human urine, has gained considerable attention over recent years. Mihelcic et al. (2011) geospatially quantified the amount of P that can be recovered from human urine and faeces, globally, regionally and by country. They concluded that if efficient systems for collecting urine and proper handling are in place, P recovered from urine and faeces could account for 22% of P demand in 2050. The amount of P available from urine in 2009 was estimated to be 1.68 million metric tons. This value is expected to increase by 2050 based on population studies to approximately 2.16 million metric tons. Kirchmann and Pettersson (1995) quantified the amounts of nutrients that are found in urine, per person per year, to be 2.5-4.3 kg nitrogen (N), 0.7-1.0 kg P and 0.9-1.0 kg potassium (K). These values are higher than the nutrient content excreted via faeces namely 0.5-0.7 kg N, 0.3-0.5 kg P and 0.1- 0.2 kg K (Kirchmann and Pettersson, 1995). These values imply that separating urine from faeces might be beneficial, considering the greater pre-treatment (energy) required for faeces so as to reduce their pathogen load. Thus by source-separating urine, 60-90% of nutrients that are ingested can be recovered in solution (Kirchmann and Pettersson, 1995). However, the amount of P from urine varies depending on the diet. Thus the amount of P from urine will be less in developing countries due to their poor diet while it will be higher in developed countries (Mihelcic et al., 2011).

Various technologies that have been evaluated to extract nutrients from human urine (Maurer et al., 2006), including using urine directly as a fertilizer and converting urine to struvite. Struvite ($CaMgNH_4PO_4.6H_2O$) was identified in waste water as early as 1930 (Maurer et al., 2006) and it

is one of the most promising nutrient recovery products from urine. Struvite, is easy to handle due to its compactness, is odourless, and the nutrient content is consistent compared to that of urine (Tilley et al., 2011). The pathogen and contaminant content of struvite is much lower than that of urine (Decrey et al., 2011). It thus provides a better and safer alternative to using urine as a fertilizer. It has received considerable attention in the literature with regards to its nutrient content and production. Work that has been done so far has been mainly related to its precipitation and laboratory production. Not much work has been carried out to evaluate struvite as an agricultural amendment and thus a gap exists between the production and the use of struvite. Generally, struvite can act as both a slow-release fertilizer (magnesium phosphate, $MgHPO_4$) and as an easily soluble ammonium phosphate ($(NH_4)_2\ PO_4$) and as such it is considered to have a considerable market potential (Maurer et al., 2006).

In order to assess the ability of struvite as a P fertilizer, nutrient release patterns through incubation studies are required, so as to understand the rate at which nutrients are being released and the amount of nutrients being released over time. To understand the behaviour of the released P, adsorption studies are required so as to understand the dynamics and fate of the P, and parameters which can be extracted from P adsorption models are necessary. To assess the effectiveness of the released P it is also essential to evaluate the P uptake by plants and its effects on yield. Since fertilizers behave differently on different soils, it is essential to test struvite effectiveness in soils of contrasting properties.

The broad objectives of this study were therefore to:

(a) assess the nutrient release patterns of struvite;

(b) study P dynamics and fate of P released by struvite;

(c) evaluate the effect of soil properties on P released by struvite;

(d) assess the effectiveness of struvite as a P fertilizer compared to a conventional P

1.1 Dissertation structure

Chapter 2 reviews the literature on the benefits and limitations of the use of human urine as a fertilizer, and the benefits of adopting struvite as an alternative management practice.

Chapter 3 describes the soils and struvite used and the methods used for their characterization.

Chapter 4 describes the incubation studies and the resulting nutrient release patterns for P, and to a lesser extent for Mg, from struvite added to the three contrasting soils. The dynamics and fate of released P from struvite through P adsorption studies are also discussed.

Chapter 5 describes the effect of struvite on plant (maize) nutrient uptake and biomass yield in a pot trial.

Chapter 6 is a general discussion on the agricultural implications and the potential and possible limitations of struvite as an alternative P fertilizer. The chapter also includes the overall conclusions on the capability of struvite as an alternative P fertilizer and the gaps for future research.

CHAPTER 2

USE OF HUMAN URINE AND STRUVITE PRODUCED FROM SOURCE SEPARATED URINE AS AN AGRICULTURAL AMENDMENT: A REVIEW

2.1 Introduction

Human excreta are a "resource" and are ubiquitous in all societies. Agricultural practices currently greatly underestimate the value of this 'free' resource. The use of human and animal faeces is an ancient practice and has overshadowed the potential use of urine in agriculture (Heinonen-Tanski and Wijk-Sijebesm, 2005). There are several benefits associated with the use of urine as an agricultural amendment such as the low numbers of pathogens in urine and the high amounts of some plant nutrients compared to faeces (Heinonen-Tanski and Wijk-Sijebesm, 2005). This combination allows for ease of handling of the urine while at the same time improves the efficiency of nutrient recycling.

This review will cover the following topics:

- the process of separating urine from faeces and the utilization of urine as a fertilizer material;
- the challenges associated with the utilization of urine as an agricultural amendment;
- an alternative management strategy for urine i.e., struvite production and the subsequent benefits of adopting struvite as an alternative management strategy;
- the crop response to struvite and the properties of soil that might affect struvite effectiveness as a P fertilizer i.e., pH, ionic strength, metal oxides and clays, and organic matter.

2.2 Urine separation and utilisation as a fertilizer material

Urine separation from faeces is the initial step in safe handling of urine for agricultural purposes. This is practiced so as to maintain the quality of the effluent to enhance the efficiency and sustainability and to reduce the health risks associated with human waste recycling (Karak and Bhattacharyya, 2011). The results of Schonning et al. (2002), had shown that most *E. coli* and certain sterols such as coprostanol are due to faeces contamination, and separating urine from the faeces reduces this risk. To separate urine from faeces a model of ecological sanitation (ECOSAN) urine diverting (UD) toilets has been developed by Larsen and Gujer (1996). There are several different types of UD toilet models and designs but they can be broadly categorized into two i.e., urine diverting dry toilets (UDDT) and UD flush toilets (Figure 2.1 a and b), with the preference differing with location and conditions, such as available water supply (Von Munch and Winker, 2011). There are several other types of UDDT such as those with two dehydration vaults, those with shallow pits and those with composting vaults. There are further differences in seat design and squatting pans and in some cases special designs might be required (Figure 2.2). Several factors determine the seat design, such as the development of the anal wash seat design which can be attributed to cultural background, or the availability of water which determines whether it will be a dry or wet system.Human urine diversion toilets have been successfully used in many developing and developed countries such as China, Ecuador, El Salvador, Ethiopia, Finland, Germany, Guatemala, India, Mexico, South Africa, Sweden, Thailand, Vietnam, and Zimbabwe (Larsen et al., 2001).

(a) (b)

Figure 2.1: Urine diverting toilet (a) wet system and (b) dry system (Langergraber and Muellegger, 2005; Kvarnstrom, 2006).

Traces of heavy metals are common in source-separated urine and faecal cross contamination has been found to be the major contributor (Jonsson et al., 1997). Studies conducted by Ronteltap et al. (2007) showed that the majority of heavy metals such as cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb) precipitate as carbonates and hydroxides (Udert et al., 2003; Ronteltap et al., 2007) during the storage of urine, thus they are less available. Under hydrolyzed conditions at pH 9 the phosphate precipitates with all available Ca and Mg ions resulting in a decrease in the soluble phosphate concentration. Ronteltap et al. (2007) also showed that the concentrations of metals in urine were lower by several orders of magnitude compared to commercial fertilizer (2:3:2; N:P:K) per microgram of P or N (Table 2.1). However, currently there are no specific threshold values for metal pollutants available for urine or urine derived fertilizers (Pronk et al., 2006).

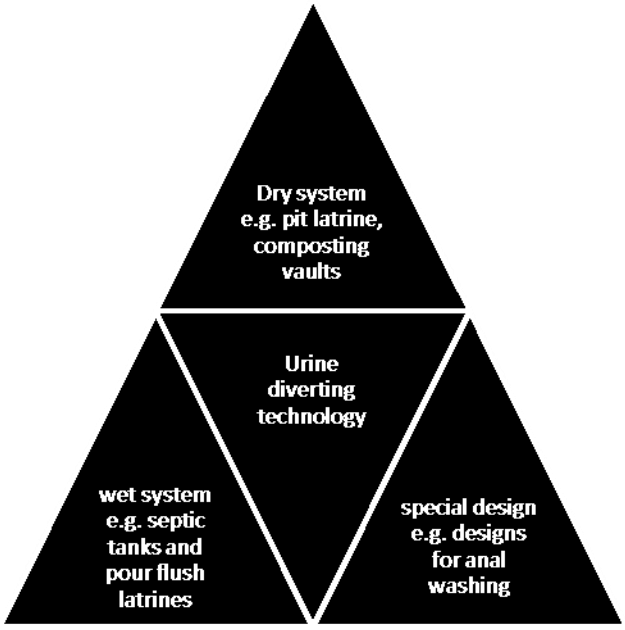


Figure 2.2: Urine diverting toilet technologies (Von Munch and Winker, 2011).

Under hydrolyzed conditions at pH 9 the phosphate precipitates with all available Ca and Mg ions resulting in a decrease in the soluble phosphate concentration. Ronteltap et al. (2007) also showed that the concentrations of metals in urine were lower by several orders of magnitude compared to commercial fertilizer (N:P:K; 2:3:2) per microgram of P or N (Table 2.1). However, currently there are no specific threshold values for metal pollutants available for urine or urine derived fertilizers (Pronk et al., 2006).

Most of the studies on the use of urine as a fertilizer that have been conducted to date conclude that the use of human urine as a fertilizer is comparable to and in some cases can outperform conventional fertilizer (Figure 2.3; Table 2.2)

Table 2.1: Concentrations of metals (x) relative to nitrogen (µg/gN) and phosphorus (µg/gP) content measured in urine, fertilizer and manure (Ronteltap et al., 2007)

Metal	Urine		Fertilizer (NPK)		Manure (Dairy)	
	$\mu g_x/g_P$	$\mu g_x/g_N$	$\mu g_x/g_P$	$\mu gx/g_N$	$\mu g_x/g_P$	$\mu g_x/g_N$
Cd	6.9	0.4	41	115×10^3	16.1	25
Cr	29.2	2.2	415	38.5×10^3	57	573
Co	31.4	2	21	1008	3.1	311
Cu	387	33.6	20	**	**	17.3×10^3
Ni	288	22.8	100	17×10^3	23.8	996
Pb	45.4	2.9	29	2648	6.2	274
Zn	667	50	410	157×10^3	390	23.8×10^3
Al	1168	66.5	**	**	**	**
Fe	654	44.2	**	**	**	**

** = below detectable concentration

In South Africa studies conducted by Mnkeni et al. (2008) used urea as the conventional fertilizer and applied urine based on the recommended N. Their results showed that urine can be a good source of N especially for cabbage and spinach, and the dry matter yield of cabbage and spinach was higher when fertilized with urine compared to urea, although maize yields were lower when urine was applied compared to urea. Similar observations have been made in several parts of the world (Table 2.2)(Heinonen-Tanski et al., 2007; Pradhan et al., 2007; Akpan-Idiok et al., 2012).

The use of urine appears to be suitable worldwide for a range of different agronomic and horticultural crops (Table 2.2) and there are no known limits that have been identified with regards to its effectiveness. A possible explanation for these observations, especially those which are based on the amount of N applied, is that the available N in the urine could remain longer in the soil compared with conventional fertilizer, as it is usually observed that the initial growth of conventionally fertilized crops outperforms that of urine (Figure 2.3) but that the final yields of urine fertilized plots usually outperform those of conventional fertilizer. There are some additional benefits which have been noted with using urine as a fertilizer such as a reduction in pest damage on cabbage (Pradhan et al., 2007). These authors hypothesized that many insects,

for example the diamondback moth, flea beetle, and mustard beetle, prefer to feed and reproduce on commercial NPK-fertilized cabbage plants.

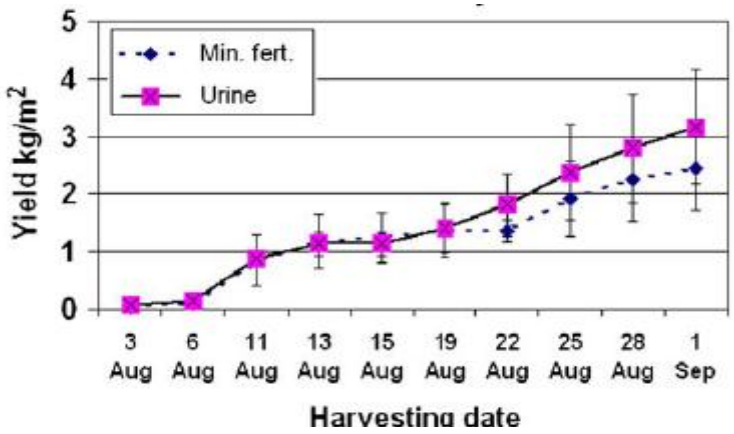


Figure 2.3: Cumulative cucumber yields (kg m^{-2}) using urine or mineral (NPK) fertilization (Heinonen-Tanski et al., 2007).

Table 2.2: Yield comparison of plants treated with urine and conventional fertilizer

Type of crop	Biomass		App based on		Country	References
	Urine	Conventional	N	P		
Cabbage (kg $head^{-1}$)	4.7	4.3	**		Finland	Pradahn et al.(2007)
Okra (g $plant^{-1}$)	20.1	19.92	**	**	Nigeria	Akpan-Idiok et al. 2012)
Tomato (g $plant^{-1}$)	90	91.8	**		South Africa	Mnkeni et al. (2008)
Maize (g pot^{-1})	536	446	**		South Africa	Mnkeni et al. (2008)
Banana (kg $bunch^{-1}$)	10k	11k	**		India	(Sridevi et al., 2009)

**= application of urine and conventional fertilizer were based on that specific nutrient;.

2.3 Challenges of using urine as a fertilizer material

Socio-cultural perspectives are the major barriers to the use of urine diversion latrines, as for example in Sweden, where full scale (about three thousand households) urine diversion toilets had been installed (Hellstrom and Johansson, 1999). The user's attitude towards the system played a crucial role in determining the success of the system. According to a questionnaire conducted by Berndtsson (2006), in Sweden, 26% of respondents were uninformed about the system, 60% found the use of the system (UD) uncomfortable (for reasons unspecified) and 77% of the respondents said theywould never buy food produced using urine or urine-derived fertilizer, knowingly. Although this study was carried out in Sweden, the lessons learned on thisproject need consideration wherever such systems are to be installed. Another major concern which was encountered in Sweden was how to integrate this new technology into existing technical and administrative infrastructure and legal regulations. Major legal and administrative barriers existed with the implementation of this system as, for example, conventional sanitation systems are generally a municipal responsibility whereas the operation of urine diverting latrines is usually the user's responsibility (Berndtsson, 2006).

In South Africa, existing sanitation policies (DWAF, 2001) are more conducive for the development and implementation of source separation of urine. However, according to a survey conducted by the Council for Scientific and Industrial Research (CSIR, 2011) in the three provinces of KwaZulu-Natal, North West and Northern Cape, 86% of the respondents using UD toilets did not like using them due to seat design and accuracy required when urinating or defecating, 32% did not know how to use them, while 16% of the household toilets were not being used for their intended purposes (some were being used as sheds, for example). One of the main conclusions from this study was that a wide gap has to be closed between the social and technical aspects of this innovation to ensure success.

Besides socio-cultural concerns, there are other factors governing the adoption of urine as a fertilizer material. One of the drawbacks associated with urine separation is quality deterioration during storage. Considerable amounts of N are lost through ammonia volatilization, which greatly compromises the quality of urine as an N fertilizer. Hellstrom et al. (1999) showed that within 45 days of storage 63% of the N was lost through volatilization, and after 100 and 222

days amounts of 83% and 96% of the N was lost, respectively. Acidification of urine with 100 mmol of sulfuric or acetic acid has been reported to extend the storage life of urine for 100 more days (Figure 2.4) (from beginning of storage to the day of application) with a minimal loss of nitrogen (Hellstrom et al., 1999). However, there is controversy on the use of this technique (urine acidification) as the major losses of N occur not during storage but during the field application of the urine (Rodhe and Johansson, 1996). Thus, the optimum effect of acidification can be assessed by the net drop in pH during spreading rather than the pH of urine during storage. This is further confirmed by the results of Hellstrom et al. (1999) who showed that a single dosage of acid at the beginning of storage is more effective at preserving N than multi dosages at regular intervals during storage. Studies conducted by Hanaeus et al. (1996) showed that an increase in storage temperature exacerbated the loss of ammonia but that the temperature effect is minimized when the urine was acidified.

The explanation of the acidification effect on preserving N is that N in fresh urine is in an organic form as urea ($CO(NH_2)_2$). Urea hydrolysis is catalyzed by the enzyme urease which many organisms possess, and this hydrolysis of urea results in the formation of ammoniacal N and an increase in pH that ultimately leads to a loss of N through ammonia evaporation (Alexander, 1977). Thus, acidification is intended to reduce the viable count of microorganisms and so minimizes urease activity and ultimately reduces N loss.

Pathogens, pharmaceuticals and heavy metals are common contaminants found in human urine, and hence use of human urine and products derived therefrom might pose potential health risks and soil contamination hazards. A study conducted by Hoglund et al. (2002) to evaluate the viral and pathogenic bacterial persistence in source-separated urine established that urine stored at 20^{o}C for six months can be considered free from *Rhesus rotavirus* and *Salmonella typhimurium* contamination. The effect of temperature in inactivating enteric viruses is a function of the type of virus. Thus, the results are only applicable for the above-mentioned viruses and environmental conditions.

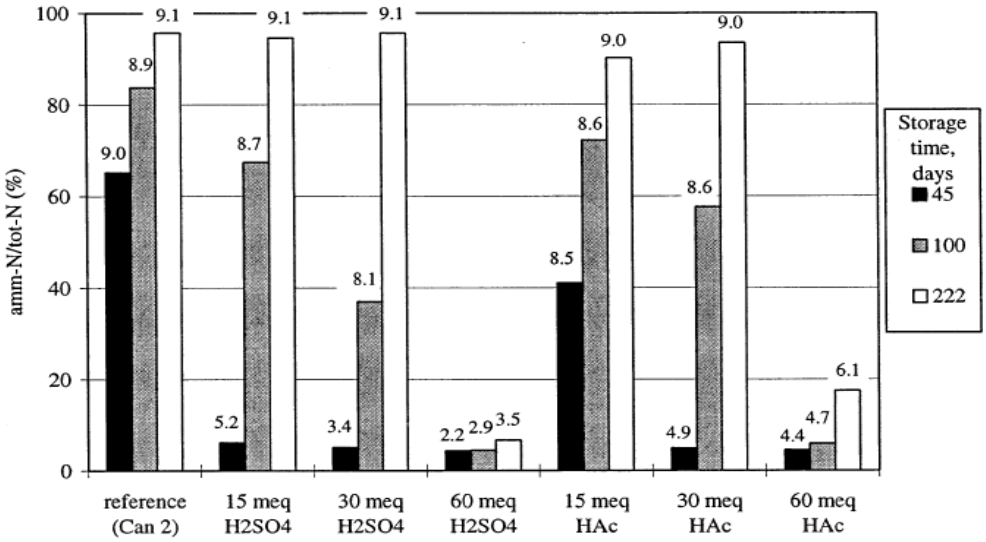


Figure 2.4: The decomposition of urea during urine storage treated with different acids of different concentration; the pH of urine during sampling times is shown above each column(Hellstrom et al., 1999).

Can 2 refers to the storage can in which the urine was stored and HAc refers to acetic acid.

The large quantity of N lost from urine especially during storage and application and difficulties in managing the resource due to its bulkiness suggest that alternative urine management strategies are required. The production of struvite from urine appears to be an attractive option. The solid state of struvite provides ease of handling with regards to storage and transportation (Etter et al., 2011). The production of struvite has been further demonstrated to reduce the pathogen risk that is usually associated with the handling of human urine (Decrey et al., 2011).

2.4 Struvite as an alternative urine management strategy

Struvite is magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$) at a molar ratio of (1:1:1) (Mg: NH_4: PO_4), a biogenic mineral with a solubility of 0.2g L^{-1} in water (neutral pH ≈ 7) and with the phosphate component entirely citrate soluble (Bridger et al., 1962). Struvite contains 5.7% N, 12.6% P and 9.9% Mg by weight. Struvite can be used as a slow release fertilizer (magnesium phosphate, $MgHPO_4$) (Johnston and Richards, 2003). Gaterell et al. (2000) suggested that modifications can be done to struvite so as to produce "enhanced struvite". The modification suggested results in a product which contains two types of fertilizer; a slow release fertilizer ($MgHPO_4$), and an easily soluble ammonium phosphate ($(NH_4)_2HPO_4$). The chemical

and physical properties of struvite make it a promising agricultural amendment (Johnston and Richards, 2003).

The precipitation of struvite is triggered by the addition of Mg (Figure 2.5) in the form of MgO, or $Mg(OH)_2$, or $MgCl_2$ or bittern (the magnesium-rich brine from table-salt production). The choice of the Mg source plays a crucial role in determining the quality and the cost of production of struvite and hence the cost of the final product (Etter et al., 2011). For a case study done in Nepal, it was established that the cheapest method of struvite production will depend on the costs related to the Mg source and its quality (amount of impurities and the total Mg content). The recovery of P from urine can be as high as 98% with a Mg dosage of 1.8 mol Mg per mol of P (Etter et al., 2011). There is no pH pre-adjustments required to the urine since the pH (8.5) of hydrolyzed urine is suitable for struvite precipitation (Buchanan et al., 1994) and the nucleation and precipitation start as soon as the Mg is added to the urine. Precipitation and crystallization of struvite can recover simultaneously phosphorus, ammonium nitrogen and magnesium as magnesium ammonium phosphate (MAP) (Figure 2.5), through Equation 2.1 (Liu et al., 2008):

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4.6H_2O \text{.....Equation 2.1}$$

For the above reaction to occur urea must be completely hydrolyzed to NH_4^{+} and this alters the pH thus leading to a decrease in the PO_4^{3-} - P concentration (Udert et al., 2003). According to Udert et al. (2003) if the temperature is maintained at 25^{o}C and urease is added with sufficient mixing, complete urea hydrolysis can occur within one day.

In order to optimize P elimination efficiency during struvite crystallization it is desirable to obtain larger particle sizes which are easier to separate and less prone to wash-out than smaller particles (Ronteltap et al., 2010). The particle size of struvite varies from 36 to 136 µm, with an average of 90 µm. According to Ronteltap et al. (2010), the main parameters which affect struvite particle size are pH and temperature. The maximum supersaturation is attained between pH 9 and 10, which corresponds well with the minimum crystal size. The maximum particle size is attained at a lower pH of 7.5 and at a lower temperature (20^{o}C). Thus with the pH of typical hydrolyzed urine being 8.5, it is not possible to achieve the maximum particle size.

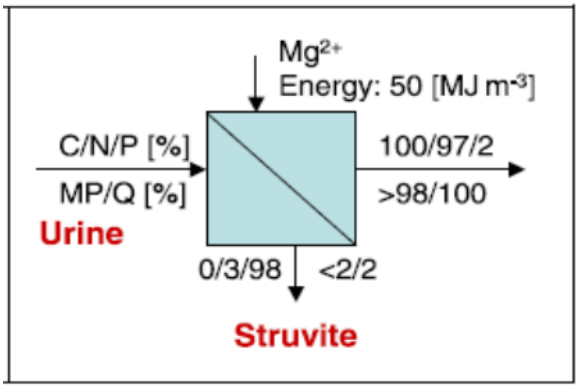


Figure 2.5: General template for struvite production (Maurer et al., 2006).

Description: flow schemes illustrate the fluxes of carbon (C), nitrogen (N), phosphorus (P), micro-pollutants (MP) and volume (Q) in percentage during struvite production. Magnesium is added for struvite crystallization to occur which is given as a final product as a downward pointing arrow below Mg^{2+} addition. Values on the left downward pointing arrow 0/3/98 (%) refer to carbon, nitrogen and phosphorus, respectively, and those on the right refer <2/2 (%) to micro-pollutants and volume, respectively.

2.5 Benefits of using struvite as an alternative management strategy: Effects of struvite production on urine volume reduction, N losses, pathogens and pharmaceuticals

Despite the potential for the use of raw human urine there are some major concerns which need to be considered. Among these is the large volume of urine that is required to adequately fertilize fields. This poses a major obstacle with regards to the energy efficiency of the system considering the storage, transportation and spreading of urine. Further, there is the hygiene factor associated with the presence of enteric viruses, pharmaceuticals and heavy metals especially during the application of urine and these might threaten human health (Lind et al., 2001). The balance of plant nutrients in human urine further hampers its use, as it contains nutrients as highly diluted compounds. The major compounds are sodium chloride (NaCl) that may cause soil sodicity, and urea ($CO(NH_2)_2$) while the rest of the nutrients such as P and Ca are present in a diluted form (Altman and Dittmer, 1994). Thus, struvite as a proposed alternative is supposed to greatly reduce these drawbacks associated with raw urine use.

There are several techniques which have been proposed for volume reduction and nutrient concentration in urine such as freezing and thawing, evaporation and reverse osmosis (Maurer et al., 2006). Struvite production reduces the urine to 2% of the original volume and captures the

majority of the nutrients P (>90%) and the added Mg (Figure 2.5) (Tilley et al., 2011). Thus, struvite provides an alternative which eliminates the poor energy efficiency associated with human raw urine and the handling problems.

The nutrient content of urine is subject to variability depending on factors such as handling and diet of the producers and thus there is no consistency in the nutrient content of the urine. Struvite on the other hand has a consistent nutrient content. The major nutrient in struvite is P, as more than 2000 mg N L^{-1} remains in the solution during struvite precipitation (Tilley et al., 2011). Nonetheless, the value of the P is currently estimated to be twice that of the N and three times more than that of K, thus making struvite a feasible option as P fertilizer. During struvite precipitation N recovery can be enhanced to 60% of the total initial N through the use of zeolite and/or activated carbon (Ganrot et al., 2007) with zeolite being preferred due to cost related issues. Zeolite acts as a cation exchanger and absorbs the remaining NH_4^+. The effectiveness of this N recovery method is directly related to the amount of zeolite used. However, using more zeolite can compromise the financial feasibility of the recovery.

The pharmaceutical, heavy metal and pathogen content of human urine are a matter subject to controversy although as outlined earlier (Section 2.3) there is no imminent threat with regards to these hygiene and safety compromising contaminants. The crystallization of struvite from human urine seems to eliminate most of these questionable health compromising contaminants.

The heavy metal content of urine is far below that found in conventional fertilizer (Table 2.1). There are no detectable amounts of heavy metals in struvite crystallized from human urine (Ronteltap et al., 2007). Even when heavy metals are added artificially to urine before precipitation, 80% of the heavy metals remain in solution with 20% in solid form. Thus, with the low initial heavy metal content in urine, struvite precipitation further lowers the content of heavy metals. The study conducted by Ronteltap et al. (2007) in assessing the behaviour of pharmaceuticals using estron (E1), estradiol (E2) and ethinylestradiol (EE2) concluded that only small amounts of pharmaceuticals attach to struvite crystals after precipitation while 99%, 97%, 95% and 100% of propranolol, E1, E2 and EE2, respectively, remained in solution. Further rinsing of the struvite crystals reduce the content of these pharmaceuticals even further.

The urine of a healthy person can be considered sterile. However, due to cross contamination and infections some pathogens can be expected in human urine and hence in fertilizers derived

therefrom (Feachem et al., 1983). Decrey et al. (2011) investigated the fate of pathogen indicator phages ΦX174 and *Ascaris suum* eggs during the production of struvite from source-separated urine. They found that the concentration of phages was similar in both the struvite and the urine and that *Ascaris* eggs accumulated within the solid phase during the precipitation and filtration process. Subsequent air-drying of the struvite partially inactivated both microorganisms. However, viable *Ascaris* eggs and infective phages were still detected after several days of drying. The even distribution of phages between urine and struvite was attributed to their size (27nm) and thus a filter fabric could not retain the phages. Thus, storage and pre-treatment of human urine still plays a crucial role with regards to pathogen control.

2.6 Struvite use as fertilizer and its effects on crop growth and nutrient uptake

Studies that have been conducted to evaluate struvite effectiveness as a fertilizer include those by Antonini et al. (2012), Cabeze et al. (2011) and Ryu et al. (2012), all suggesting that struvite can be as effective as or better than commercial fertilizer (Figures 2.6 and 2.7). Antonini et al. (2012) used struvite produced with different Mg:P ratios and commercial triple superphosphate (TSP) fertilizer as the reference P source with application rates of struvite based on P. They obtained results which were conclusive with regard to the ability of struvite to supply and improve plant uptake of P (Figure 2.7). Initially there was a higher (but not statistically significant) P uptake from the TSP treatments compared to struvite but for the second trial there was a significantly higher P uptake from struvite treated pots compared to TSP pots (Figure 2.6). The trends for plant biomass (g pot^{-1}) of this trial were identical to those of P uptake (Figure 2.6). It was concluded that struvite is more effective on a long-term basis compared to conventional fertilizer.

The explanation for these observations can be related to Neumann and Romheld's (2012) findings that in the case of sparingly soluble P sources, P deficiency triggers roots to excrete acid which enhances P solubility of the source, in this case struvite, thus improving P availability, as all of the P in struvite is citric acid soluble. There are a significant number of micronutrients and essential nutrients (K, Na, S, Fe and Ca) at levels near 1% (w/w) and this composition imparts a further positive quality to struvite which extends beyond just recovering P and N compared to conventional P fertilizer (Gell et al., 2011). Similar observations have been made by Cabeze et

al. (2011), although their trial was performed using struvite produced from different sewage treatment plants. They concluded that struvite can be as effective as triple super-phosphate (TSP), even in soils of contrasting properties (Figure 2.7).

Cabeze et al. (2011) explained these observations similarly, but opposite to Antonini et al. (2012) since the latter considered the water solubility of struvite to be the major driving parameter of effectiveness, whereas Cabeze et al. (2011) considered the lower purity (presence of other nutrients) of struvite to be the major driving force in obtaining positive results from struvite.

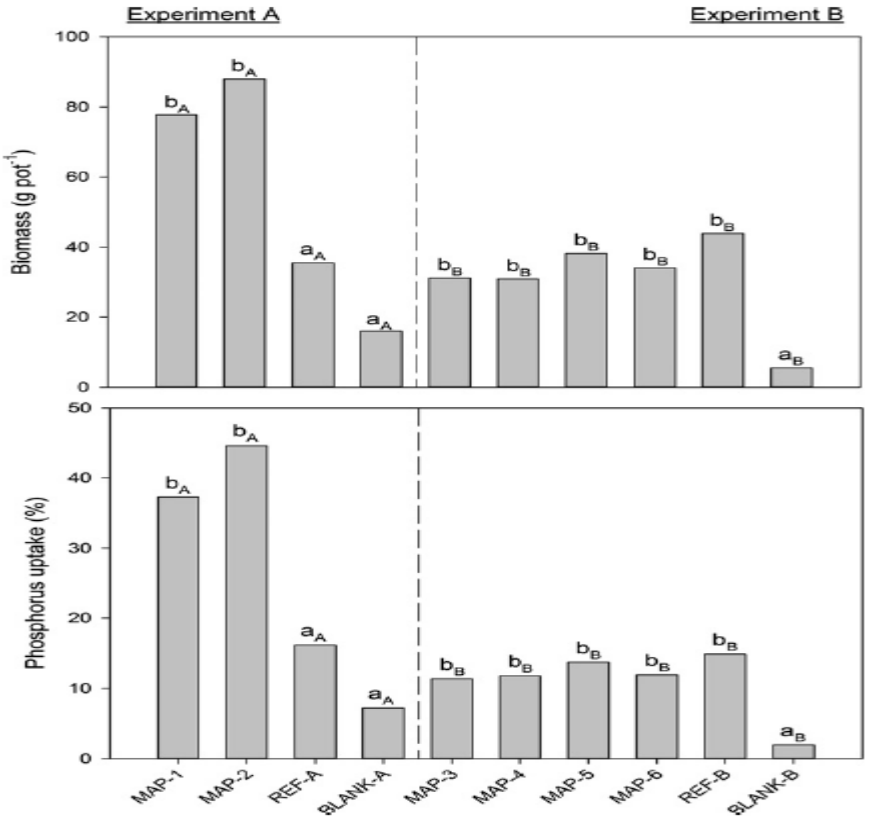


Figure 2.6: Phosphorus uptake (%) and biomass of maize (*Zea mays*) as affected by Ref=TSP; and MAP=struvite (Antonini et al., 2012).

Experiment A harvested 82 days after sowing and experiment B harvested 51 days after sowing. The lower case letters represents statistically significant differences according to the Scheffe test at the p = 0.05 level. MAP-1= sediments from storage tank which is connected to waterless urinal; MAP-2 = struvite precipitated from undiluted urine by addition of MgO; MAP-3 = struvite precipitated from diluted urine by addition of MgO; MAP-4 = Struvite precipitated from undiluted urine by circulation through a filter bag containing MgO; MAP-5 = Struvite precipitated from undiluted urine by MgO addition; MAP-6 = Struvite precipitated from undiluted urine by MgO addition; REF-B= triple superphosphate; BLANK-B = Blank.

Thus, due to the impure nature of struvite that included other essential nutrients, even though it has a lower solubility than TSP it manages to be as effective as TSP and under certain conditions to outperform TSP. The higher efficiency of struvite under acidic conditions was accredited to its improved solubility.

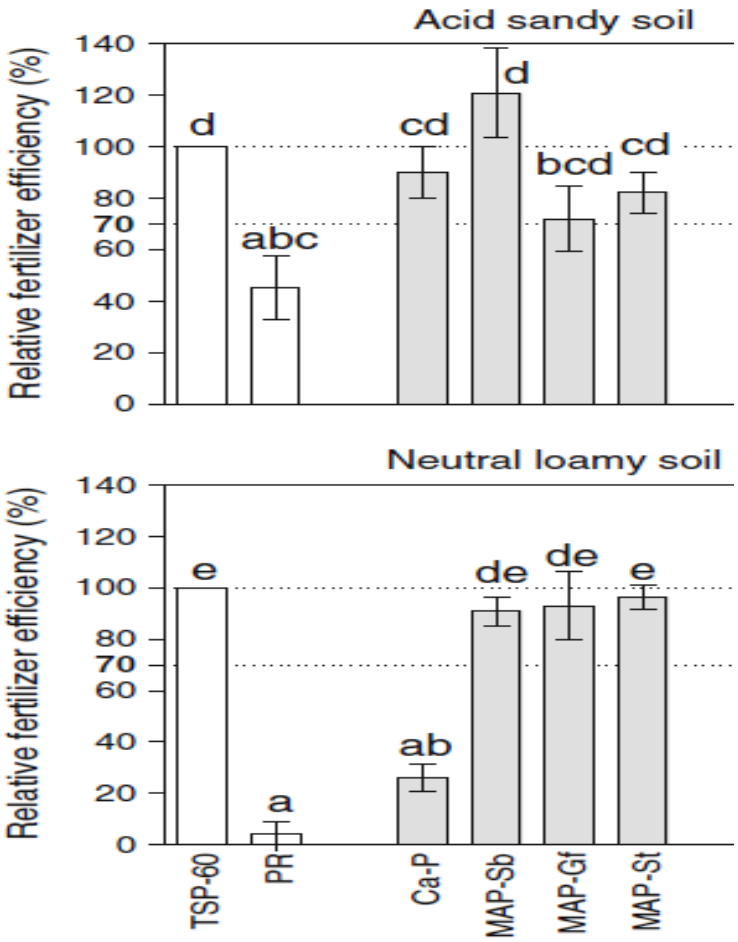


Figure 2.7: Relative fertilizer efficiency of recycled calcium phosphate (Ca-P),(PR), triple superphosphate (TSP-60) and struvite from three different sewage plants (MAP-Sb, Gf, St) on the growth of maize in two contrasting soils (Cabeze et al., 2011).

Different letters denote significant differences between treatments at the $p \leq 0.05$ level. TSP= triple superphosphate; PR= rock phosphate (unspecified); Ca-P= calcium phosphate precipitated from municipal waste; MAP-Sb/Gf/St= struvite precipitated using material from different sewage treatment plants of Seaborne (Sb), Gifhorn (Gf) and Stuttgart (St).

Similar observations regarding the potential of struvite have been made by Ryu et al. (2012) who showed that there is a growth improvement of Chinese cabbage with an increase in struvite application rates (Figure 2.8).

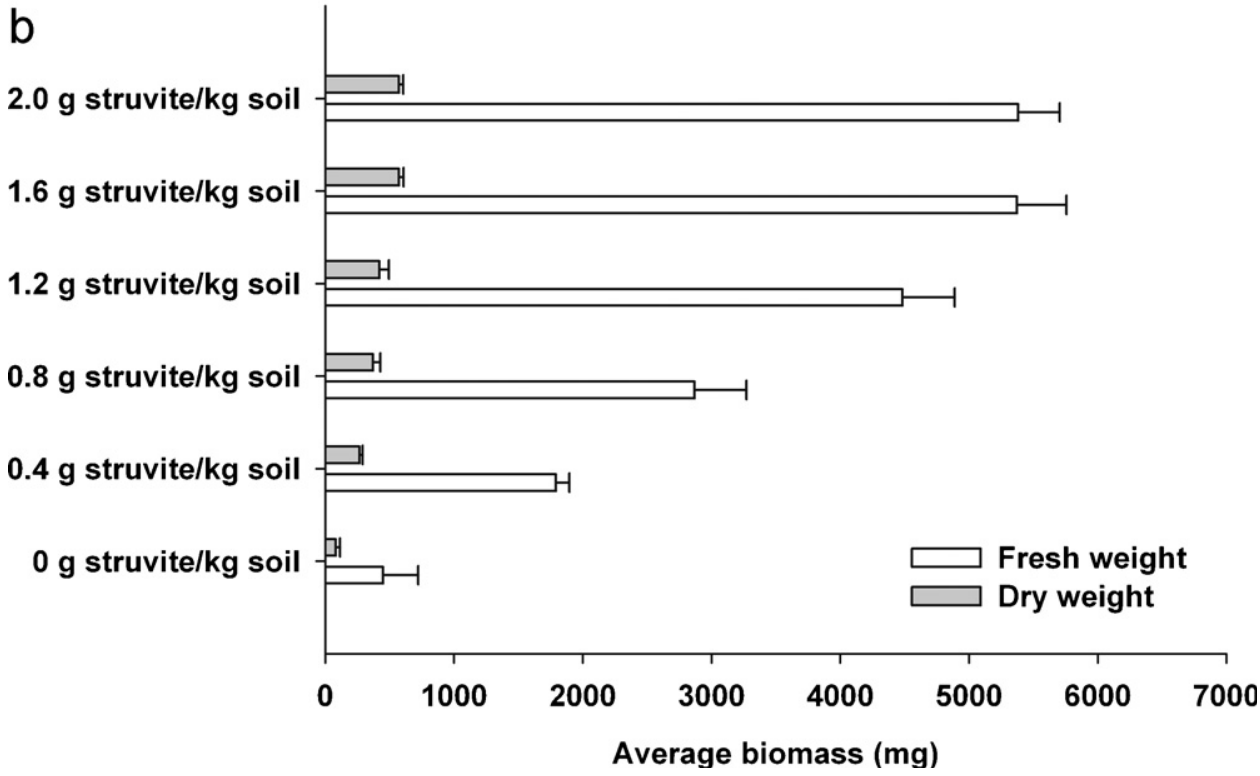


Figure 2.8: Biomass variation of Chinese cabbage 42 days after planting as a function of struvite application rates (Ryu et al., 2012).

2.7 Soil properties that affect the effectiveness of P released from struvite.

Soil properties and the availability of water are the major determining factors on the effectiveness of fertilizer aside from its chemical composition. Upon application, a fertilizer is subject to various reactions, some improving its effectiveness and some hampering effectiveness. Thus, soil properties are as important as the inherent chemical properties of the fertilizer in affecting the effectiveness of an amendment. A substantial body of literature exists on the

chemistry of different P sources. It is probable that the chemistry of struvite P to some extent will behave similarly to other P sources, although this hypothesis has not been proven currently

Several soil properties have been studied to assess their effect on P chemistry. These include, but not limited to, pH (Arai and Sparks, 2001), organic matter (Sibanda and Young, 1986), ionic strength (Liu et al., 2011), iron and aluminium oxides (Borggaard, 1983), clay mineralogy and content (Edzwald et al., 1976) and soil physical properties (Ullah et al., 1983). This section reviews some of these properties and to infer, where applicable, their potential effect on P released from struvite.

2.7.1 pH

Soil pH has a direct double effect on struvite P effectiveness as it affects both struvite solubility and the subsequent P dynamics in the soil. The solubility of struvite in a pure system has been shown to be highly pH dependent. Generally the solubility of struvite is inversely related to pH i.e., it decreases with an increase in pH (Doyle and Parsons, 2002). As the pH increases there is an increase in phosphate ion concentration and a decrease in ammonium concentration due to the reduction of protons in the system. Further, pH determines the speciation of Mg^{2+}, NH_4^+ and PO_4^3 (Bhuiyan et al., 2007). However, the effect of pH on the solubility products and thermodynamic properties of struvite have limited direct implications in explaining the effectiveness of struvite as a P fertilizer. The soil pH is mostly influential in P dynamics related to P retention and sorption. Some studies have suggested that the effect of pH on its own on P dissolution and availability is insignificant and that its major implications are related to P sorption (Kanabo and Gilkes, 1987; Bolan et al., 1988). Kanabo and Gilkes (1987) suggested that the improvement in P dissolution from rock phosphates is due to the fact that acidity is a common attribute of soils that have high P sorption capacity which consequently improves the solubility and nutrient release in such soils. It is likely that the same principle might be applicable to struvite.

It is generally accepted that phosphorus adsorption decreases with increasing pH, so that an inverse relationship exists between pH and phosphate adsorption (Willet and Cunningham, 1983; Arai and Sparks, 2001; Weng et al., 2012). The adsorption of P is a function of surfaces with variable charge (metal oxides and broken edges). The charge of a hydroxyl surface can be

positive, neutral or negative depending on the pH. The protonation one site/two pK model has been proposed by (Parks, 1965) so as to explain the development of a charge on these sites with variable charge (Equations 2.2 and 2.3).

$$MeO^{1-} + Hs^{+} \leftrightarrow MeOH^{0} \text{.....} \quad \text{Equation 2.2}$$

$$MeOH^{0} + Hs^{+} \leftrightarrow MeOH^{+} \text{.....} \quad \text{Equation 2.3}$$

Where Me refers to the generic surface sites and the charge of the site denoted as superscript on the above equations.

As the pH decreases; the electrostatic potential in the plane of adsorption of P increases, leading to an increase in P affinity and hence adsorption. The increase in P adsorption consequently leads to an increase in P dissolution and availability if a P source is present in the soil matrix following the solubility product principle. It is for this reason that in highly acidic soils there might be a temporary improvement in P availability upon addition of a soluble P source.

The effectiveness of struvite is expected to be higher in acidic soils as there are more protons available for dissolution and solubilisation of the struvite. As low pH is often an attribute of soils with higher P affinity due to higher P sorption, soils with low pH are expected to enhance struvite solubility and hence P release although this P may only be temporarily available.

2.7.2 Ionic strength

Struvite solubility in a pure system increases with an increase in ionic strength, due to the resultant decrease in the effective concentration of the component ions of struvite (Bhuiyan et al., 2007). Thus, in soils with a high electrolyte concentration it is expected that struvite solubility will be improved and hence its effectiveness will be improved.

The P adsorption is directly proportional to the ionic strength (Wang et al., 2009). The presence of counterions such as Na^{+} or K^{+} or any other cations which increase with an increase in electrolyte concentration makes the adsorption plane less negative thus improving phosphate adsorption through increasing the electrostatic potential at the plane of adsorption. As Barrow et al. (1980) concluded an increase in ionic strength is similar to a drop in pH which also increases

the electrostatic potential in the plane of adsorption. Wang et al. (2008) also made a distinction with regards to the contribution of various cations in improving P adsorption whereby it was observed that there was an improvement in P adsorption when the electrolyte was higher in K^+ than Na^+. The explanation for this observation was that soils have higher affinity for K^+ than Na^+. It was also found that P adsorption was further improved with an increase in divalent cations in an electrolyte.

2.7.3 Organic matter

The general mechanism by which organic matter (OM) binds phosphate is considered to be ternary complexation whereby Fe(III) or Al(III) play the role of a bridging cation between phosphate and organic matter (Bloom, 1981; Gerke, 2010). Soil pH plays a vital role in organo-metal interaction, as OM adsorbs strongly to metals at low pH and the adsorption decreases with an increase in pH. Ternary complexation can be expressed as P-Fe-OM or P-Al-OM. Complex stability is inversely proportional to the stability of the metal-OM interaction, implying that phosphate can only be assimilated into the complex up to a certain threshold, and beyond that threshold the complex collapses. It was on the basis of this mechanism that Borggaard et al. (1990) suggested that OM plays an insignificant role in P dynamics.

Ternary complexation is one of several explanations for phosphate/organic matter interaction. Iron (III) reduction as impacted by OM is another important interaction. This is achieved by microbial reduction of Fe, Fe mobility, and Fe mineral formation prevention (Cornell and Schwertmann, 1996). Organic matter influences the Fe (III) reduction through electron shuttling (Jiang and Kappler, 2008) that alters the structure of Fe minerals by sorption, complexiметric dissolution or by impeding crystallization. Organic matter is redox active and Fe(III) is among the elements that can be reduced by organic matter. When Fe(III) is reduced it releases some of its occluded P thus improving P availability to plants. Several researchers have observed an increase in P availability in the presence of OM and it is on the basis of this mechanism that Sibanda and Young (1986) suggested a decrease in P adsorption in the presence of organic matter.

2.7.4 Iron and aluminium oxides and clay mineralogy

Iron oxides are the components of soil which have been given much credit for phosphate adsorption and availability. Borggaard (1983) concluded that a close correlation exists between phosphate adsorption and clay and aluminium oxides. It exists because of the close correlation that exists between these components and iron oxides, making iron oxides the most important component with regards to phosphate availability.

The generally accepted mechanism by which phosphate is adsorbed by iron oxides involves ligand exchange. Two single coordinated hydroxyl groups or water molecules are replaced by one phosphate molecule (Torrent, 1997). Parfitt and Russell (1977) using spectroscopic methods identified the type of complex which is formed by phosphate and the surface of goethite and hematite, and concluded that an inner-sphere complex was the primary sorption mechanism by which phosphate is retained on the surface. Thus soils with high iron oxide content could be expected to chemically sorb the P released from struvite.

The role of clay minerals in P adsorption can be attributed to the expanding lattice (Murphy, 1939). This happens through water entering the lattice as hydrated cations, and through this mechanism some phosphate might also enter between the layers. However, phosphate entering through this mechanism is not strongly retained as it can be easily leached by water. These observations suggested that phosphate adsorbed in this manner does not form permanent bonds with the unit, but rather it is held by weak electrostatic forces of attraction. This is contrary to kaolinite, which has exposed OH groups on the surface and ligand exchange occurs, forming a permanent bond between phosphate and the unit. This, however, does not imply that kaolinite adsorbs more phosphate than montmorillonite. Edzwald et al. (1976) stated that anion exchange does not play a major role in P adsorption, when the study is conducted on pure synthetic clay minerals. High P adsorption by montmorillonite can be attributed to the high amount of calcium associated with this mineral, thus forming a stable calcium phosphate precipitate. Specific surface area also plays a very significant role. To a certain extent it is expected that clay mineralogy will play a role on the dynamics of P released from struvite with its availability depending on the type of clay minerals present.

2.8 Conclusions

There is potentially a threat to the future supply of phosphorus and consequently to food security. In order to mitigate this threat a variety of responses are required and closing the nutrient loop through human waste recycling is one of the promising answers. Faeces treatment and health risks compromise the financial feasibility of using them as an agricultural amendment. The majority of the nutrients (90%) are located in the urine and thus separating urine from faeces might provide a viable and efficient system. If this was to be successful an estimated 22% of P demand could be met through urine reuse. The use of human urine as an agricultural amendment is associated with several limitations. Processing human urine to struvite (reducing its bulkiness and some of the health concerns) provides a solution to some of the more problematic urine properties. Struvite can be considered to be mainly an alternative P source, with the presence of other essential nutrients, such as N and Mg, being essentially an added bonus, giving it a potential competitive advantage over conventional P fertilizers. The low amount of heavy metals, an inherited property from urine, further enhances the quality of struvite. Comparisons can be drawn between struvite and conventional P fertilizer in their agronomic usage and studies show that struvite, under certain conditions, can outperform conventional fertilizer, or at least fairly compete with it. The P released from struvite is expected to be governed by the same soil properties that are governing the P released from conventional P fertilizer and therefore many of the same factors which are taken into consideration when applying commercial P fertilizer will hold true for struvite. In general, it can be concluded that struvite is potentially a viable agricultural amendment, as there are no major reported problems associated with its use.

However, there have been no investigations conducted in South Africa on the use of struvite as an agricultural amendment and so this study is to investigate the potential of struvite as an alternative source of P for crop growth. Although, as indicated earlier, struvite also supplies N, Mg and other elements that are necessary for plants, this study will focus on P since this is the major element in struvite and is the element which is most likely to be in short supply in the not so distant future.

CHAPTER 3

MATERIAL DESCRIPTION AND CHARACTERIZATION

3.1 Soils

Three contrasting soil types were used, namely a Cartref (Cf) E horizon and the A horizons of an Inanda (Ia) and Sepane (Se) (Soil Classification Working Group, 1991). The three soils were chosen so as to represent a wide range of properties. The Cf was sampled from near Ottos Bluff near Pietermaritzburg (29°56′59″S, 30°38′22″E) under virgin veld. The Ia was collected from World's View (29°57′49″S, 30°57′49″ E), Pietermaritzburg under commercial forestry and the Se from a permaculture site at Newlands-Mashu (29°77′6″ S, 30°99′27″E), near Durban. All soils were air-dried and sieved to pass a <2mm mesh before use. The Ia, with a humic A horizon, is characterized by advanced weathering, a high concentration of Al and Fe oxides and high acid saturation (Fey, 2010). The Se forms part of the Duplex soil group and is characterized by a strongly developed soil structure, high clay content in the subsoil and a high base saturation (Fey, 2010). The Cf is a sandy soil with a low organic carbon content and low base status (Fey, 2010).

3.1.1 Soil analysis

Soil pH was determined in both water and 1M KCl at a soil: solution ratio of 1:2.5 using pH meter PHM 210. The exchangeable acidity, acid saturation, exchangeable Ca, Mg, K, and extractable P were determined by the Fertilizer Advisory Service of the KwaZulu-Natal Department of Agriculture, Forestry and Fisheries, Cedara following methods in the Standard Soil Testing Handbook of The Non-Affiliated Soil Analysis Working Committee (1990). Extractable Al (Al_d) and Fe (Fe_d) in the soil samples were extracted by the dithionite-citrate-bicarbonate method (DCB) (Mehra and Jackson, 1960). Poorly crystalline forms of these elements (Fe_o and Al_o) were determined by the selective extraction method using acid ammonium oxalate (Jackson et al., 1986). Soil texture was determined by the pipette method (Gee and Bauder, 1986), clay mineralogy by X-ray diffraction (Bühmann et al., 1985), and

organic carbon (OC) percentage by dichromate oxidation (Walkley, 1947) respectively, (Dr I Bame, pers.comm.).

3.1.2 Soil characteristics

As expected the Ia had a high concentration of both DCB and oxalate-extractable Fe and Al. Exchangeable acidity and acid saturation were high, with values of 3.32 cmol L^{-1} and 83%, respectively (Table 3.1). The exchangeable acidity of the Se was low and the same as that of the Cf. Organic carbon was highest in the Ia, followed by Se and Cf. The Ia had a loam texture while the Se was a clay loam and the Cf a loamy sand. Total bases were highest in Se, followed by much lower values in the Ia and Cf, with values of, 18.35 cmol L^{-1} for Se and 4.01 and 2.45 cmol L^{-1} for Ia and Cf, respectively.

Table 3.1: Some characteristics of the soil used

Parameters		**Soil form and horizon**		
		Inanda (A)	**Sepane (A)**	**Cartref (E)**
pH	H_2O	4.74	7.14	6.26
	KCl	3.95	5.99	5.17
Exch acidity (cmol L^{-1})		3.32	0.09	0.09
Acid Sat (%)		83	0	4
org C (%)		7.54	1.92	0.18
Fe (%)	DCB	2.95	1.84	0.26
	Oxalate	1.84	0.64	0.18
Al (%)	DCB	0.89	0.17	0.01
	Oxalate	0.52	0.23	0.032
P (mg L^{-1})		12	6	3
K (mg L^{-1})		38	117	58
Ca (mg L^{-1})		86	1896	316
Mg (mg L^{-1})		20	1033	77
Total bases (cmol L^{-1})		4.01	18.35	2.45
Sand (%)		29.9	21.4	80.2
Silt (%)		48.2	42.9	12.9
Clay (%)		21.9	35.7	6.9
Illite (%)		0	5-20	5-20
Kaolin (%)		20-60	5-20	20-60
Goethite (%)		5-20	<5	<5
Anatase (%)		0	0	<5
Gibbsite (%)		0	20-60	0
Sample density (g mL^{-1})		0.77	1.15	1.42

3.2 Struvite

The struvite used throughout this study was produced at a pilot plant by the Pollution Research Group, Discipline of Chemical Engineering at the University of KwaZulu-Natal, Durban Campus. The struvite, produced by the addition of $MgCl_2$ to human urine sourced from UD toilets within the eThekwini Municipality, was crystallized, the suspension filtered, and the struvite retained on the filter was dried under ambient conditions for at least four days.

3.2.1. Struvite analysis

The particle size distribution of the struvite was determined by passing a known mass (10g) through a nest of 500, 250 and 106 µm sieves. Struvite solubility tests were conducted in 50 mL distilled water in duplicate at application equivalent to 0, 0.1, 0.2, 0.5, 1, 2, 5, 20, 30 and 60 g struvite L^{-1}. The suspensions were shaken on an end-over–end shaker for 2 hours, centrifuged at 3500 rpm (Sorvall RC 5C; Heraeus; Model-930437) for 15 minutes, and then filtered through a Whatman number 1 filter paper. Phosphorus in the extracts was determined by the molybdenum blue method (Murphy and Riley, 1962). Magnesium and Na in the extracts were analysed by atomic absorption spectrophotometry (AAS, Varian SpectraAA-200), and NH_4-N was determined by the evaporation distillation method (Okalebo et al., 2002), followed by titration with 0.02M HCl. The pH was measured using pH meter PHM 210, and EC using EC meter CDM 210.

3.2.2 Struvite properties

The struvite used was a pale yellow in colour due to the material not being completely dried during the production process. The colour could have been removed by further washing and drying but this was not done to prevent loss of elements from the material.The struvite showed a distinct bimodal distribution of particle size, with 59% of particles less than 106 µm and 35% greater than 500 µm (Table 3.2).

Table 3.2: The particle size distribution of the struvite used

>500 µm mesh	500-250 µm mesh	250-106 µm mesh	<106 µm mesh
----------%----------			
35	3	3	59

The struvite showed appreciable water solubility (Table 3.3). At 0.1 g struvite L^{-1}, solution concentrations of P, N, Mg and Na were 13.8%, 8%, 9.4% and 6%, respectively (Table 3.3). The values obtained thus approximated those of the theoretical solubility of 12.6 % P, 5.7 % N and 9.9% Mg. Above 0.1 g L^{-1}, although the elemental concentrations in the solution increased, they increased at a declining rate more prominent between 0.1 and 5 g L^{-1} and 20-60 g L^{-1}. At 20 g L^{-1} where the amounts of P, Mg and Na were about double those at 5 g L^{-1}. At low rates, the struvite dissolves presumably due to the very low solid:solution ratio and releases ammonium that could have formed ammonium hydroxide, which raises the pH with little effect on EC (Appendix 3.1). At higher rates less struvite dissolves due to the sufficiently high pH and higher solid:solution ratios and so less ammonium hydroxide is formed having less effect on the final pH. However, the other elements released, perhaps especially Na and Mg, raise the EC. This view is perhaps further confirmed by the strong correlation between Na and EC (Table 3.4).

Table 3.3: Struvite solubility properties in water

Struvite	pH	EC	P	N	Mg	Na
(g L^{-1})		(µS cm^{-1})	----------(mg L^{-1})----------			
0.1	9.69	86.3	13.85	8.0	9.40	5.98
0.2	9.68	132	17.77	9.8	10.54	23.5
0.5	9.45	179	18.25	10.2	11.85	26.9
1	9.57	203	18.45	10.1	15.50	28.9
2	9.54	259	20.40	12.0	12.55	29.5
5	9.21	702	22.35	13.1	14.05	32.7
20	8.74	1290	43.69	12.0	22.73	85.4
30	8.58	2450	50.50	12.7	22.18	120
60	8.31	over range	59.70	24.4	35.80	179

Further a positive relationship as determined using Microsoft Excel 2010exists between EC and application rate of struvite and a strong negative correlation exists between pH and EC (Tables 3.3 and 3.4). Although there is a substantial body of information regarding the effect of pH and

EC on struvite solubility, there is very limited information regarding the effect of struvite on pH and EC although these are considered to be the master variables that control struvite solubility (Doyle and Parsons, 2002; Bhuiyan et al., 2007). The strong correlation that exists between EC and application rate (r^2 = 0.97; Table 3.4) confirms the dissociation of elemental constituents of struvite which increases the ionic strength. The fall in pH with increase in struvite application rate (Table 3.3; r^2 = 0.86;, Table 3.4) might be explained by its limited solubility at higher application rates, as the elemental concentrations increased at a declining rate when related to the application rate. This notion is further perhaps supported by the pH value at 0.1 g L^{-1} as it was the highest, and at this application rate the solubility should be at a maximum. This further perhaps explains the release of the elements from struvite, as Massey et al. (2009) have shown that struvite solubility decreases with an increase in pH.

Table 3.4: Some correlations between struvite solubility properties in water

Variables	Curvilinear	r^2 values
P vs Mg	Linear	0.90
P vs N	Linear	0.97*
P vs Na	Linear	0.96
Rate vs P	Logarithmic	0.91
Rate vs Mg	Linear	0.95
Rate vs Na	Linear	0.97
Rate vs EC	Linear	0.97
Rate vs pH	Logarithmic	0.86
P vs EC	Logarithmic	0.92
Na vs EC	Linear	0.94
pH vs EC	Linear	0.90

*linear to 5 mg L^{-1}

CHAPTER 4

PHOSPHORUS SORPTION AND NUTRIENT RELEASE (P AND Mg) POTENTIAL OF HUMAN URINE-DERIVED STRUVITE

4.1 Introduction

When struvite (magnesium ammonium phosphate) is added to soil it is expected to dissolve incongruently and release its constituents, at varying rates. Due to the presence of ammonium some change in soil pH could be expected. As indicated in Chapter 2, few studies have been conducted to evaluate the nutrient release patterns of struvite. However, there is a substantial body of information with regards to dissolution of phosphate rock (PR) (Warren et al., 2009). It is considered likely that the same soil properties such as pH and exchangeable acidity that influence the dissolution of PR will affect struvite dissolution.

Two of the major factors that influence phosphorus availability are the properties of the original P source and the properties of the soil to which it is applied (Smyth and Sanchez, 1982). The effectiveness of any P source is dependent upon its dissolution and the availability of the released P. It is essential to understand the nutrient release patterns in different soils as these will have implications for their availability. The rate of dissolution and the extent to which a mineral dissolves are governed by pH, ionic strength, initial concentration of the elements and temperature (Tang et al., 2003). The chemical composition of an amendment is crucial and the release rate of a constituent is dependent upon the solubility properties of the original product.

Magnesium can prevent the formation of a Ca-PO_4 precipitate at higher pH and may have the ability to improve P availability under calcareous and high pH conditions (Rasul et al., 2011). According to Rasul et al. (2011), P fertilizer efficiency can be improved by over 55% with a Mg application equivalent to 80 kg ha^{-1}. Similar observations had been made by Sun et al. (2006) whereby exchangeable P increased by 46.5% upon addition of 60 kg ha^{-1} of Mg. However, there is an overriding concern with regards to the Mg content of struvite as the Ca uptake by plants can be compromised if the available Ca:Mg ratio in the soil is not balanced so causing a Ca deficiency (Stevens et al., 2005). The ideal ratio is considered to be between 4:1 and 7:1 (Ca: Mg), although this varies with soil type and plant.

Sorption is one of the major processes affecting P availability to plants and soil organisms and its fate in the environment. The major factors affecting P sorption include pH, redox potential, ionic strength, metal oxides (content and crystallinity), organic matter, clay mineralogy, concentration of P (Martinez et al., 1996) and exchangeable Ca, Al and Fe (Gichangi et al., 2008). The extent of weathering and leaching of soils, and clay and organic matter (OM) contents could therefore affect the fate of P derived from struvite in soils, as indicated in Chapter 2.

The behaviour and sorption of P in soils have been studied extensively. For South African soils the studies of note are those that have been done in KwaZulu-Natal, Mpumalanga and Eastern Cape soils by Brainbridge et al. (1995), Henry and Smith (2002) and Gichangi et al. (2008), respectively. These investigations examined mainly the effect of soil properties such as pH and degree of weathering as indicated by the amount of iron and aluminium in crystalline, amorphous, and extractable forms and the variation in P sorption are mainly attributed to variability in the amount of Fe and Al. Availability of P from struvite could therefore vary as affected by these soil parameters. It is therefore essential to study the nutrient release potential of struvite in contrasting soils.

The relationship between the concentration of adsorbate and the surface of the adsorbent may be expressed by isotherms of which the Freundlich and Langmuir isotherms are most often used (Mesquita et al., 2002). The governing (underlying) equation of the Langmuir isotherm is:

$$Q = \frac{Q_{max} KC}{1+KC} \quad \text{.....Equation 4.1}$$

The most common linearized Langmuir equation is:

$$\frac{C}{Q} = \frac{C}{b} + \frac{1}{Kb} \quad \text{.....Equation 4.2}$$

where Q is the amount of solute sorbed; K is the affinity constant for adsorption; C is the concentration of the solute at equilibrium; and b is the maximum amount of the solute that can be adsorbed.

If the Langmuir equation is used accurately it can successfully estimate the maximum adsorption (Taylor et al., 1996). Further information about the chemical mechanism of the sorption can be deduced from the Langmuir equation (Bubba et al., 2003).

For soils which have no well-defined upper limit of sorption, the Freundlich isotherm (Equations 4.3 and 4.4), is usually used.

$$Q = K_f C^n \quad \text{..... Equation 4.3}$$

The following linearized form of the equation is commonly used:

$$\log Q = n \log C + \log Kf \quad \text{.....Equation 4.4}$$

where Q is the amount of solute sorbed; n is a correction factor; K_f is the distribution coefficient; and C the equilibrium concentration.

The external P requirement (EPR) is one of the parameters which is used to assess the P requirements of plants it takes into account the P sorption properties of the soil (Dodor and Oya, 2008). The EPR determines the amount of P (Q) required to give a specific equilibrium concentration (C). It uses an adsorption equation in a form of Q=mC+ y and after substituting for the desired equilibrium concentration of P (C), the amount (Q) required can be calculated from the equation. A value of 0.2 mg L^{-1} of P in solution is considered a standard P concentration at which plant growth is not limited by P (Fox and Kamprath, 1970). Although this is often regarded as the P concentration in soil solution at which plant growth is not limited, it varies with soil type and crop and thus lower equilibrium concentrations such as 0.1 and 0.05 mg L^{-1} are also used (Gichangi et al., 2008).

The fate of P from source (fertilizer) to plant is controlled by several factors. Williams (1967) discussed these as an intensity factor (a factor related to the P concentration in soil solution), a quantity factor (labile P), a capacity factor (phosphorus buffering capacity of the soil), and a mobility factor. There is a paramount relationship that exists between the intensity, quantity and capacity factors. As the intensity factor decreases, for example, due to sorption or plant uptake, the P in the solid state (quantity factor) dissolves, obeying the solubility product principle since P movement is controlled by a concentration gradient (diffusion). Hence the quantity factor decreases and the buffering capacity of the soil increases and approaches a maximum as the

intensity factor approaches zero (Shirvani et al., 2005). The objectives of the present experiments were to determine:

- the P sorption characteristics of the soils, and their effect on P released by struvite; and
- theMg and P release patterns of struvite.

It was hypothesized that the P and Mg content will increase with an increase in struvite application and that the rate and extent of dissolution of the struvite will follow the dissolution/precipitation principle.

4.2 Materials and methods

4.2.1 Sorption studies

The sorption studies were carried out as suggested by Rayment and Lyons (2011). The equilibration P concentrations for the Ia were 0, 5, 10, 20, 40, 80, 100, 140 and 180 mg P L^{-1}, and for the Se and Cf 0, 2.5, 5,7.5, 10, 12.5, 15 and 20 mg P L^{-1}. The equilibrating solution concentrations for the Se and Cf were different from that of Ia due to the known high sorption characteristics of the Ia. The P solutions were prepared by dissolving potassium di-hydrogen phosphate in 0.01 M calcium chloride. The suspensions were shaken for 16 hours and then left to equilibrate for 2 hours at 25^{o}C. The tubes were centrifuged at 12,000 rpm (Sorvall RC 5C; Heraeus; Model-930437) for 12 min and then filtered through a Whatman No. 1 filter paper. The extract was then analyzed for P using the molybdenum blue method (Murphy and Riley, 1962).

4.2.2 Sorption isotherms

The amount of P sorbed (Q mg kg^{-1}) was taken as a difference between the amount of P added and the amount of P at equilibrium (C mg L^{-1}). Due to the Se and Cf results not fitting the Langmuir equation, the Freundlich equation was used to determine the P affinity of these soils.

The external P requirement was determined by substituting the desired values of C of 0.2 and 0.1 mg L^{-1} to the equations and solving for Q. The buffering index was taken as the slope of the

tangent of the Freundlich equation and the phosphorus buffering capacity was the slope of the tangent of the linear equation of Q against C.

4.2.3 Incubation experiments

4.3.3.1 Experimental set-up

Two incubation studies were conducted to assess the P and Mg release from struvite. In each case two kg of each soil (Ia, Se and Cf) was amended with powdered struvite, previously passed through a 500 µm mesh. The application rates are given in Table 4.1.

The first set of samples was incubated for 122 days (29 March-29 July 2012) to assess when most of the dissolution was occurring. The second set of samples were incubated for 22 days (21 August-15 September 2012) to closely monitor the changes that were occurring within that time period, as that was when most of the dissolution was found to occur in the first incubation. In this study the application rates of P were based on the P affinity of each individual soil (as derived from adsorption isotherms), as dissolution is improved in soils with high P affinity. It is for this reason that the soils have different application rates. A similar approach was used by Warren et al. (2009) in their studies on animal bone-char.

The treated soil samples were wetted to 50% of their water holding capacity (determined by saturating a subsample of known mass of each soil and allowing it to drain for 24 hours and reweighing) for the second incubation and to 75% for the first incubation. From the first incubation it was observed that 75% of water holding capacity was close to waterlogging and for this reason it was reduced to 50% of the water holding capacity for the second incubation. After the samples were wetted they were incubated in a constant temperature room at 25^{o}C. Moisture correction was done weekly after determination of weight loss, samples were opened every three days after the initial sampling period to avoid development of anaerobic conditions.

The sampling from the incubation was done on days 1, 2, 4, 8, 16, 28, 64 and 128 for the first set and on days 1, 2, 5, 8, 16 and 22 for the second set of incubation. At each sampling 50g would be removed from the container, air dried, passed through a 2 mm mesh and analyzed for various elements and pH. From the first set of incubations it was determined that certain application rates

were not required. Thus the number of application rates in the second set of incubations was reduced so as to cover the critical application rates.

Table 4.1: Application rates of struvite on the different soils for the first and second sets of incubations

	First set		Second set	
Soil	**P (kg ha^{-1})**	**Amount of struvite (g struvite kg^{-1} soil)**	**P (kg ha^{-1})**	**Amount of struvite (g struvite kg^{-1} soil)**
Ia	10	0.035	control	_
Ia	20	0.07	10	0.035
Ia	30	0.11	30	0.11
Ia	40	0.14	50	0.175
Ia	50	0.175		
Ia	60	0.21		
Se	30	0.065	Control	_
Se	60	0.13	30	0.065
Se	90	0.20	90	0.20
Se	120	0.26	180	0.39
Se	150	0.31		
Se	180	0.39		
Cf	40	0.07	Control	_
Cf	80	0.14	40	0.07
Cf	120	0.21	120	0.21
Cf	160	0.28	240	0.42
Cf	200	0.35		
Cf	240	0.42		

4.3.3.2 Analysis

Samples were analysed for pH using a Meter Lab PHM 210 pH meter with a standard glass electrode in both water and 1M KCl at a soil: solution ratio of 1:2.5. Phosphorus was extracted with 0.25 M ammonium bicarbonate, EDTA disodium salt and 0.01 M ammonium fluoride (AMBIC) solution, and analysed using the molybdenum blue method (Murphy and Riley, 1962). To analyse for exchangeable Mg (only for the second set of incubations) the soil was leached with 0.1M unbuffered NH_4Cl at a soil to solution ratio of (1:25). Soil (10 g) was transferred to a filter paper in a funnel and then leached with 50 mL of 0.1M ammonium chloride into a 250 mL volumetric flask. This leaching was repeated three more times and the flask then made up to the

mark using the NH_4Cl solution. The extract was then analyzed for magnesium by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Varian 720 ES.

4.4 Results

4.4.1 Adsorption parameters

The quantity and capacity factors (EPR and buffering index, respectively) of the soils that were used for the sorption studies showed a similar trend, with the Ia > Se > Cf. Due to the Se and Cf not fitting the Langmuir equation it was not possible to calculate their P sorption maxima. However, K_f from the Freundlich linearization, which has been found to have a positive correlation with P sorption maxima calculated from the Langmuir equation (Hussain et al., 2006), was used. The K_f values followed the trend; Ia > Se > Cf (Table 4.2). The trend for EPR was in the order; Se > Ia > Cf.

Table 4.2: Phosphorus adsorption parameters of the Inanda (Ia), Sepane (Se) and Cartref (Cf) soils

Adsorption parameters	**Soil form**		
	Ia	**Se**	**Cf**
*Buffering index (mL g^{-1})	560.49	311.42	249.7
PBC(mL g^{-1})	123	168	113
Q0.2(mg kg^{-1})	29.99	35.28	22.39
Q0.1(mg kg^{-1})	16.29	17.42	11.02
K_f Freundlich	2.79	1.98	1.51

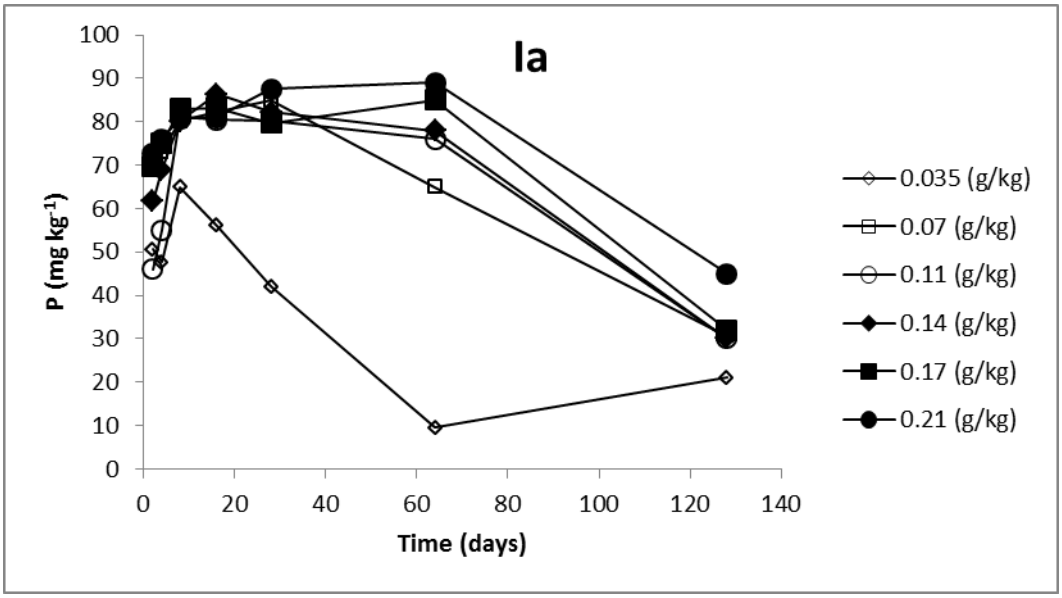
* Buffering index, the slope of the tangent of the Freundlich equation; PBC (phosphorus buffering capacity) - slope of the tangent of the linear equation Q (mg kg-1) vs C (mg L-1); Q 0.2,0.1 - initial amount of P required to maintain soil solution P concentration at levels = 0.2 and 0.1 mg L-1, respectively; K_f – the distribution coefficient.

4.4.2 Patterns of P release from struvite in different soils during incubation

During the first incubation, solution P increased with an increase in struvite application rate in all of the three soils, particularly the Ia and Cf (Figure 4.1). The highest concentration of solution P was recorded in the Ia. In that soil, solution P rapidly increased to maximum levels within the first 8 days after which it stabilised and then dropped between days 64 and 128 (Figure 4.1). On the contrary, solution P concentration in the Se and Cf rapidly increased and declined within the first 8 days, after which it stabilised up to 28 days. After 28 days solution P declined further in the Se and then remained more-or-less constant. Whereas in the Cf after day 28 a clear differentiation between the different application rates started to occur and P content increased

gradually, with the P content positively correlated to the application rate, and thus the P content increased with an increase in struvite application rate.

(a)



(b)

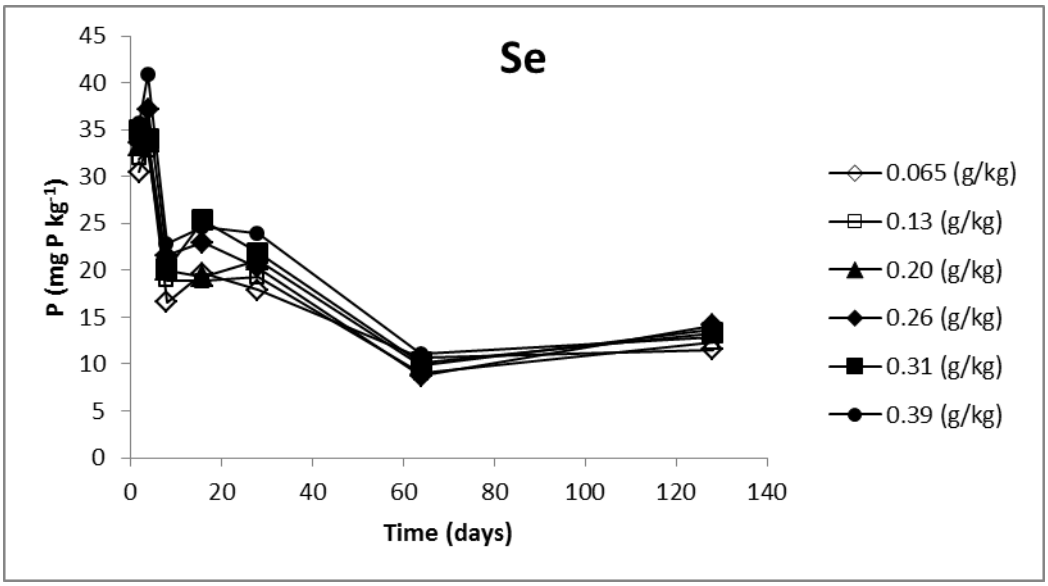


Figure 4.1: Phosphorus concentration changes during the first incubation of soils with different application rates of struvite written as legend (g of struvite kg^{-1} of soil) in (a) Inanda (Ia), (b) Sepane (Se), and (c) Cartref (Cf)

(c)

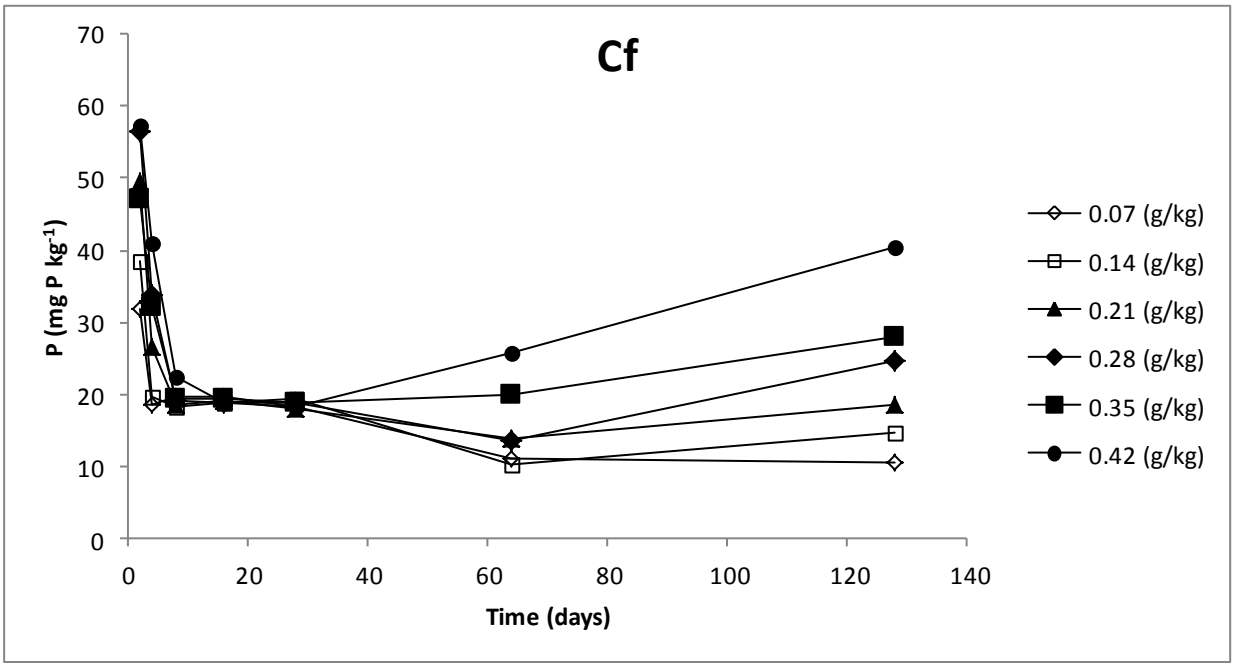


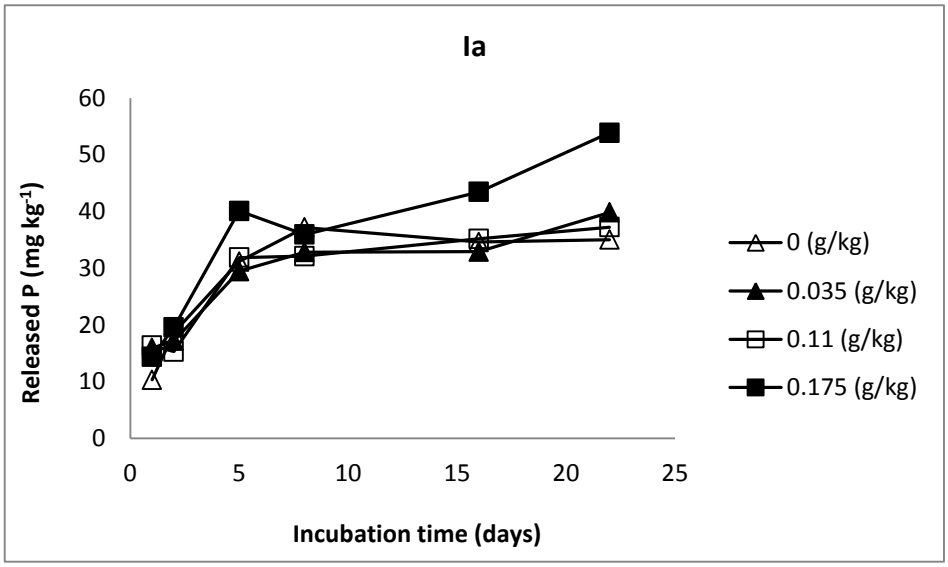
Figure 4.2 continued: Phosphorus concentration changes during the first incubation of soils with different application rates of struvite written as legend (g of struvite kg^{-1} of soil) in (a) Inanda (Ia), (b) Sepane (Se), and (c) Cartref (Cf).

In the second incubation, release of P increased with incubation time for all the treatments in the Ia and for the two highest rates in the Cf. The highest amount of P was recorded in the Ia followed by the Cf and Se, respectively (Figure 4.2). A maximum P concentration of 54 mg kg^{-1} was recorded in the Ia on day 22, while that for Se (5.5 mg kg^{-1}) was recorded on day 2, and on day 5 for the Cf (33.09 mg kg^{-1}). In the Ia and Cf, soil solution P increased with incubation time in the first 5 days, after which it remained relatively constant or increased at a slower rate (speed of P release) in Ia. In the Cf with the application rate of 0.21g of struvite kg^{-1} there was a rapid drop in P concentration from day 16 to day 22, the lowest application rate (0.07 g struvite kg^{-1} of soil) in Cf remained relatively constant during the entire incubation period.

The highest struvite application rate (0.18 g struvite kg^{-1} soil) in the Ia resulted in greater P release than the control throughout the incubation (Figure 4.2), whereas the lower rates (0.11 and 0.035 g struvite kg-1 of soil) were similar to the control up to 16 days. The response in the Se was minimal with the highest struvite rate of 0.39 g kg^{-1} releasing only 5.5 mg P kg^{-1} (Figure 4.2). Solution P concentration in amended and control Se soil was ≥10 times lower than those of

the Ia and Cf throughout the incubation period, where the application rates of struvite were similar.

(a)



(b)

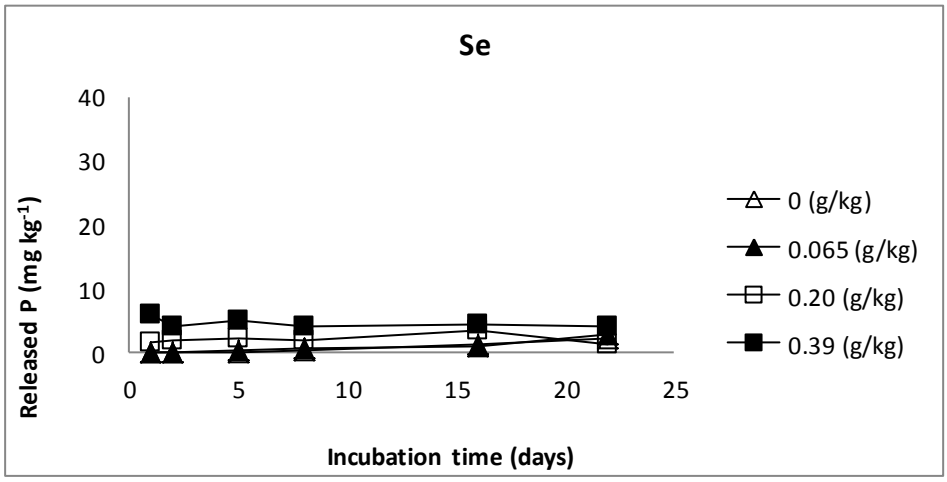


Figure 4.3: Phosphorus concentration (mg P kg^{-1}) changes during the second incubation of soils with different application rates of struvite written as legend (g of struvite kg^{-1} of soil) in (a) Inanda (Ia), (b) Sepane (Se), and (c) Cartref (Cf).

(c)

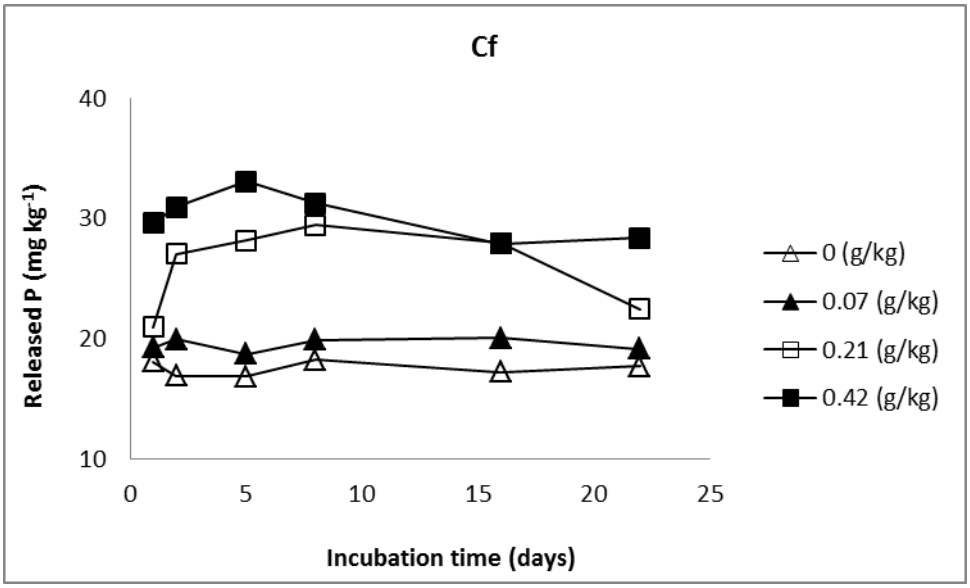


Figure 4.4 (continued): Phosphorus concentration (mg P kg^{-1}) changes during the second incubation of soils with different application rates of struvite written as legend (g of struvite kg^{-1} of soil) in (a) Inanda (Ia), (b) Sepane (Se), and (c) Cartref (Cf).

4.4.3 Patterns of magnesium release from struvite in different soils during the second incubation

The soil solution Mg concentration increased with an increase in struvite application rate particularly for the Se while for the other soils the increases were only marginal. The concentration of Mg did not respond to incubation time for all soils(Figure 4.3). Magnesium content was in the order Se > Cf > Ia throughout the incubation period. The Se soil had about 10 times higher Mg than the Cf.

(a)

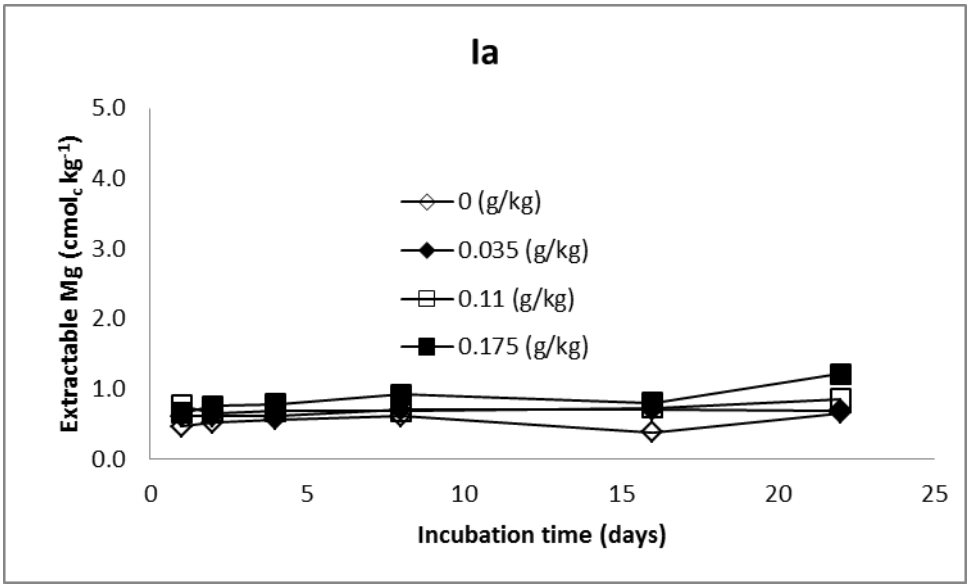
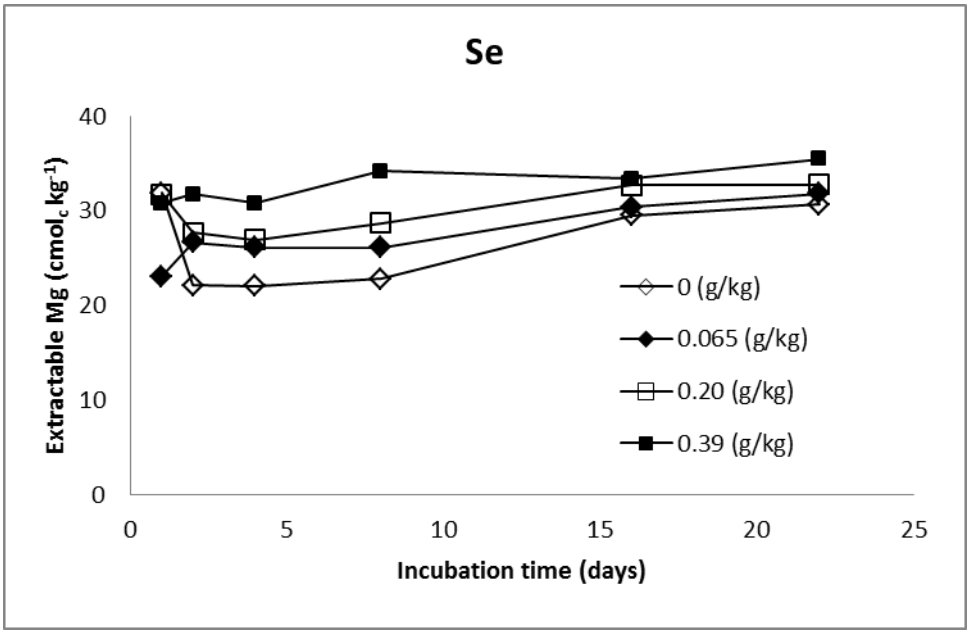


Figure 4.5: Magnesium concentration (cmol$_c$ kg^{-1}) changes during the second incubation of soils with different application rates of struvite written as legend (g of struvite kg^{-1} of soil), in (a) Inanda (Ia), (b) Sepane (Se), and (c) Cartref (Cf).

(b)



(c)

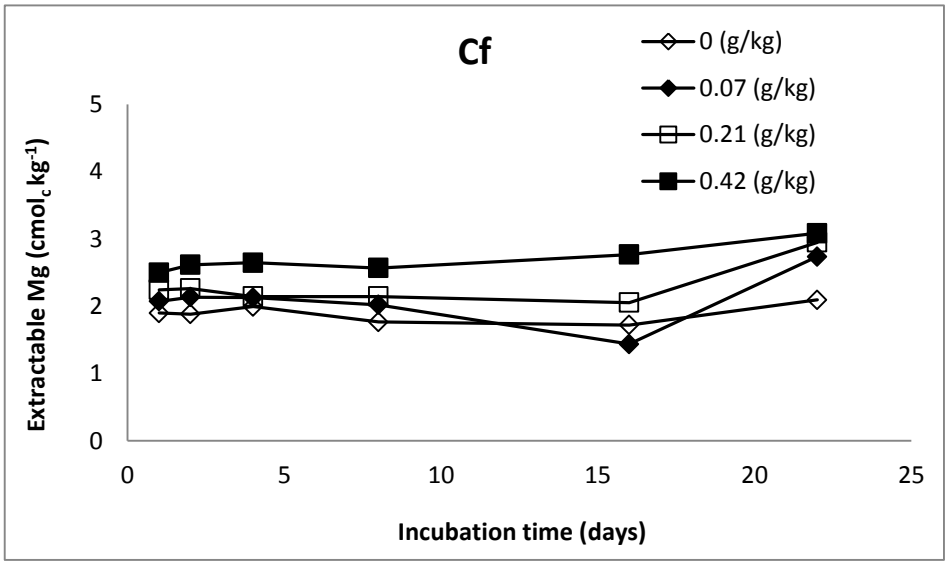
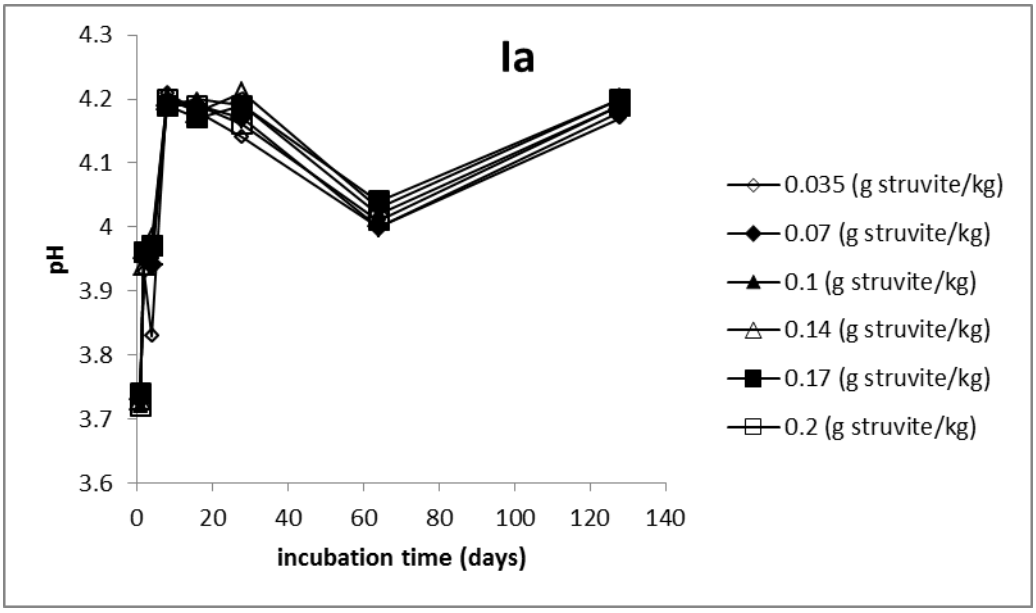


Figure 4.6 (continued): Magnesium concentration ($cmol_c$ kg^{-1}) changes during the second incubation of soils with different application rates of struvite written as legend (g of struvite kg^{-1} of soil), in (a) Inanda (Ia), (b) Sepane (Se), and (c) Cartref (Cf).

4.4.4 pH changes during first incubation

At all application rates the pH in the Ia increased by approximately 0.5 pH units in the first 16 days and remained constant thereafter. In the first 28 days there is only a minimal difference between the various application rates of struvite (Figure 4.4). However, thereafter a differentiation occurs between the various struvite application rates with the pH increase directly proportional to the application rate in the Ia. Figure 4.4 generally shows that the high application rates have relatively higher pH compared to the lower application rates. The Se and Ia were not very similar and there are clear distinctions between the rates in the Se even though they do not appear to be proportional to struvite application rates. The differentiation in pH is also clear in the Cf although the pH changes are not proportional to the struvite application rates, similar to the Se.

(a)



b)

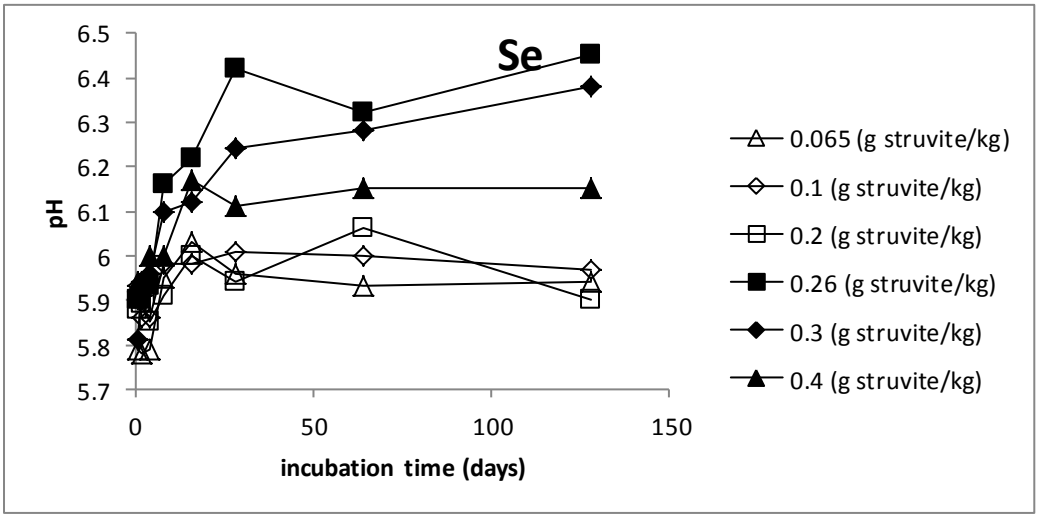


Figure 4.7: pH changes during the first incubation of soils with different application rates of struvite written as legend (g of struvite kg-1 of soil), in Inanda (Ia), Sepane (Se), and Cartref (Cf).

(c)

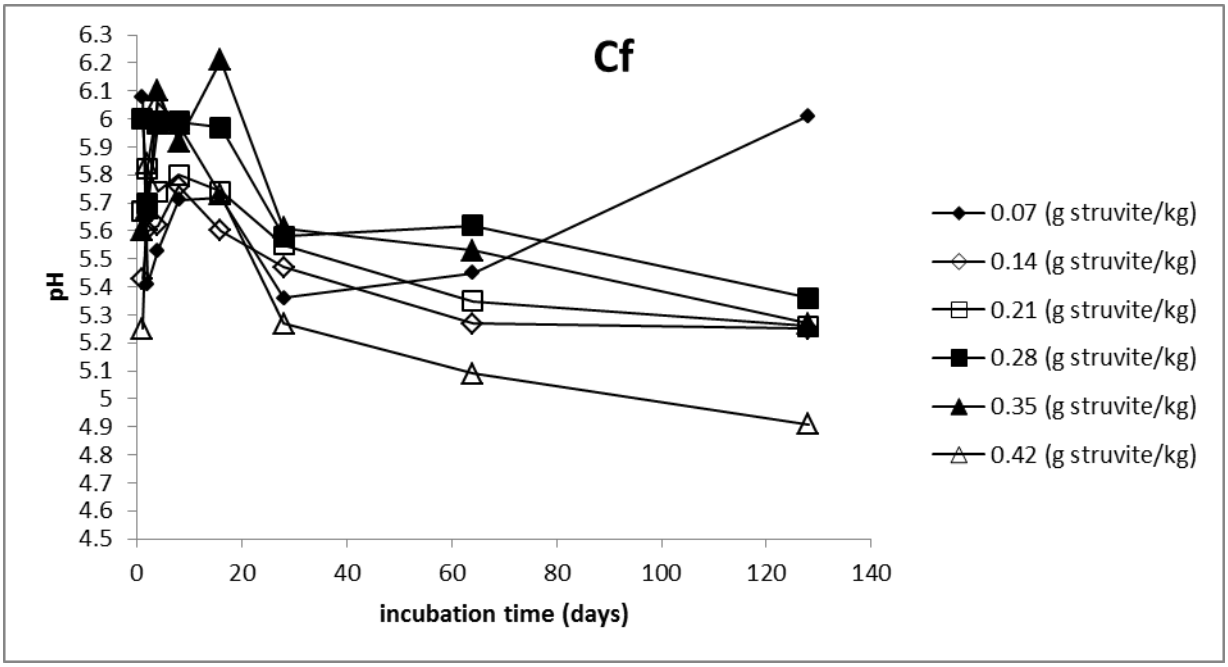


Figure 4.8 (continued): pH changes during the first incubation of soils with different application rates of struvite written as legend (g of struvite kg-1 of soil), in Inanda (Ia), Sepane (Se), and Cartref (Cf).

4.5 Discussion

The L type sorption isotherm for the Ia suggests a well-defined upper limit to P sorption (Travis and Etneir, 1981), whereas the C-type isotherms of the Se and Cf suggest constant partitioning of solute between the solution and adsorbent (Tan, 2010). The higher P sorption parameters of the Ia are probably due to its high Fe and Al content (both crystalline and amorphous) (Borggaard, 1983; Enyard, 1994; Torrent, 1997), low pH (Willet and Cunningham, 1983; Arai and Sparks, 2001; Weng et al., 2012) and its high clay content.

Precipitation-dissolution reactions are the major contributors to the P dynamics in the Cf. According to Zhang et al. (2002), P dynamics in soils with a sand content between 50 and 78%

are controlled by precipitation-dissolution reactions rather than sorption-desorption because of the limited sorption sites on sand grains. The sandy texture of the Cf explains the lower P sorption parameters compared to the Ia and Se. This is further confirmed by the soil solution P of the Cf which remained constant for the 0.07 and 0.21 g struvite kg^{-1} rates during the second incubation.

The relatively high sorption properties of the Se are probably due to its higher clay content and its higher amount of 2:1 clay minerals. There is a positive correlation that exists between P sorption and clay content due to the increase in specific surface area (Ullah et al., 1983). The lower P sorption in the Se than that of Ia is due to its lower content of Fe_d and Fe_o. The capacity factor as reflected by the PBC was higher in the Se than the Ia (Table 4.2), but the buffering index produced an opposite result. Since higher OM content reduces the buffering capacity of a soil due to the blockage of adsorption sites (Shirvani et al., 2005) it is likely that the higher OC content of the Ia contributed to its relatively lower PBC.

The quantity and capacity factors which can be studied by adsorption are much more useful in explaining the dissolution and availability (intensity) of a P source as this is the concentration which is available for plant uptake. The external P requirements for soil solution P concentration of 0.2 and 0.1 mg L^{-1} was in order of Se > Ia > Cf. The low P requirements for Cf are due to its low P retention, while the highest P requirements for Se might be due to the initially low P concentration, its high buffering capacity and higher sorption. The lower external P requirements of the Ia relative to Se (and higher than Cf) could be due to its initially higher P content, and high sorption capacity based on K_f values.

The release of P from struvite was not linear with the incubation time, as is usually the case from other P sources (Smyth and Sanchez, 1982; Kanabo and Gilkes, 1987; He et al., 2005; Nying and Robinson, 2006; Warren et al., 2009) probably due to its incongruent dissolution property and bimodal distribution of particle size (Table 3.3). The solubility properties of struvite and the properties of the individual soils are important in determining the rate of P release from the struvite. Struvite in this regards behaves more like a PR since PR effectiveness is dependent on its own properties that govern its solubility, and soil properties that control the fate of the released P (Nying and Robinson, 2006).

Dissolution of struvite decreases with an increase in pH (Massey et al., 2009). Struvite solubility in the Se could have been limited by its higher pH, resulting in low extractable P compared to Ia and Cf. This suggestion perhaps is further confirmed by results from the incubation experiments which showed minimal differences in solution P between different struvite application rates. Thus the combination of high pH and Ca in Se and high sorption and buffering capacity might have limited the availability of P in soil solution. Further, as shown in Section 3.2, struvite dissolution increases pH and this perhaps might have further intensified the limitation of struvite solubility in Se.

The low P sorption, as reflected by the K_f value of the Cf explains the high solution P concentration. The pH (in KCl) of 5.0 in the Cf has been shown not to limit struvite solubility (Massey et al., 2009). The P released by struvite in the Cf becomes available in solution resulting in clear differences between the various application rates.

The low pH of the Ia promoted solubility of the struvite, releasing P and the high initial P concentration could have resulted in the highest solution P concentration of the three soils. The high initial P concentration could explain the minimal difference between the low application rates in the Ia and the control. The continuous increase of solution P even in the control of the Ia could be due to the decomposition of the large amount of organic matter in that soil, releasing organic P through mineralization and inorganic P held on sorption sites (Sibanda and Young, 1986).

It is also important to note that the P release in all the soils was lower in the second incubation than the first and this could be a result of adjustment to lower moisture conditions for the second run. This could have affected the dissolution of struvite and demonstrates the importance of the availability of sufficient, but not excessive, moisture for maximal effect from such a low solubility P source as struvite. This is in agreement with the results presented by Kanabo and Gilkes (1988), which showed that North Carolina rock phosphate dissolution is improved under high moisture content conditions.

The liming effect in the Ia as shown by the pH measured could also have affected solution P during incubation. The change in pH during incubation is one of the most informative parameters in assessing the rate of mineral dissolution (He et al., 2005). As shown for phosphate rock, P dissolution consumes protons and thus increases soil pH (Lewis et al., 1997); this is the well-

known liming effect due to PR. Thus the rate of increase in soil P can be reflected by the rate of change in pH over time. The rapid increase of pH in the Ia by 0.6 pH units at the highest struvite application rate correlates well with the change in P concentration of the soil.

As expected struvite dissolution produced a gradual increase in Mg content in all three soils, the increase in Mg content increasing with struvite application rate. This further suggests that struvite is relatively soluble. The relatively constant Mg content in the Se might be due to its initially high exchangeable Mg. The intermediate reactions of struvite compared to SSP and PR can mitigate some of the environmental impacts associated with P escaping agro-ecosystems, while at the same time making the nutrient available, especially perhaps in acid, sandy soils.

4.6 Conclusions

The affinity of the soils for P, represented by K_f, was in the order Ia > Se > Cf. Release of P and Mg in the amended soils increased with increasing struvite application rate for Ia and Cf with only a minimal response in Se in both sets of incubations. Release of P from struvite amended soils was ten times lower while Mg was ten times higher in the Se than in the Cf and the Ia. The pH and P sorption of individual soils seem to be important parameters which determine the P release from struvite. Since pH is an important parameter in determining struvite dissolution, future studies must assess the effect of liming low pH soils on P release from struvite.

CHAPTER 5

STRUVITE AS A PHOSPHORUS FERTILIZER FOR MAIZE (*Zea mays*)

5.1 Introduction

Closing the nutrient loop through excrement (mainly urine) recycling using ECOSAN urine diverting toilets could assist in the mitigation of phosphorus shortages in agriculture and assist in the improvement of sanitation at various levels of society (Mihelcic et al., 2011). Urine separation enhances the value of the effluent, as the major nutrients in sewage are concentrated in urine and it further reduces the pathogen load of the effluent (Karak and Bhattacharyya, 2011). Although use of urine has potential as confirmed by studies conducted by Mnkeni et al. (2008) and others there are overriding concerns which often makes the use of urine not financially feasible or culturally acceptable (Chapter 2).

The use of struvite is proposed as an alternative so as to reduce some of the challenges associated with the use of raw urine. There are several trials which have been conducted in assessing the potential of struvite as a fertilizer (Cabeze et al., 2011; Antonini et al., 2012; Ryu et al., 2012; Chapter 2) all reporting positive results when struvite and conventional fertilizer are compared. Thus far there are no foreseeable or determined limitations with regards to the agronomic effectiveness of struvite. However, this has not been examined in South African soils.

Although the solubility of struvite is much lower than that of conventional fertilizer, it has been observed that maize fertilized with struvite can yield a significantly higher biomass compared to conventional fertilizer (Antonini et al., 2012), although there was no clear explanation as to how this is possible, considering the differences in solubility. Similar observations had been made by Cabeze et al. (2011). Thus, in order to arrive at a full understanding of the P dynamics of struvite it is necessary to test struvite in a wide range of soils. Due to its incongruent dissolution behaviour and that recommendations for P are based on conventional fertilizer which dissolves congruently it is necessary to test different application rates of struvite, so as to determine the lowest application rate with the highest plant response.

The objective of this study was to determine the effects of different struvite application rates on maize yield and P uptake in three contrasting soils, compared to a conventional P fertilizer. It was hypothesized that the response was going to be maximum in the soil which responded positively to the struvite during the incubation experiments. Thus the maximum struvite response was expected to be observed in the Ia, followed by the Cf and Se, respectively.

5.2 Materials and Methods

5.2.1 Pot experiment

The experiment was conducted at the University of KwaZulu-Natal (UKZN), Pietermaritzburg Campus (29^{o}36'S, 30^{o}23'E) under glasshouse conditions with maximum and minimum temperatures of 26^{o}C and 16^{o}C, respectively. Each of the soils (Chapter 3) was treated with different rates of P using struvite as the P source. Struvite was mixed with 2 kg of soil which had been air-dried, milled and passed through a 2 mm sieve. The application rates were based on P requirements of maize as recommended by the KwaZulu-Natal Department of Agriculture, Forestry and Fisheries. The application rates for each soil were chosen so as to include no fertilizer, half the recommended rate, the recommended rate and twice the recommended rate. The recommended application rates were 20, 60 and 80 kg P ha^{-1} for the Ia, Se and Cf, respectively. The target maize yield for the recommended rates was 12 t ha^{-1}. These converted to rates of 0.20, 0.40 and 0.42 g of struvite per pot for the Ia, Se and Cf, respectively. Some of these rates were used in the first incubation experiment (Chapter 4) i.e., (20 kg ha^{-1} for Ia and 60 and 80 kg ha^{-1} for Se and Cf, respectively). For the Ia the rates used were thus 0, 0.10, 0.20 and 0.40 g struvite per pot; for the Se 0, 0.20, 0.40 and 0.80 g struvite per pot; and for the Cf 0, 0.21, 0.42 and 0.84 g of struvite per pot. Single superphosphate (SSP; 10.5%P) was used as the reference fertilizer and was applied at the recommended application rate for each soil as a positive control.

After subtracting the amount of N applied as struvite the balance was applied as urea for the N requirements of 200 kg ha^{-1} for all three soils. The amount of urea applied to the Ia, Se and Cf was 0.35, 0.20 and 0.16 g per pot, respectively. Laboratory grade KCl was used to supply K. For the Ia the K required was 205 kg ha^{-1} (0.35g per pot); for the Se 10 kg ha^{-1} (0.010 g per pot); and for the Cf 100 kg of K ha^{-1} (0.085 g per pot), respectively. The experiment was set up as a 3 x 4

randomized block design with three soils and four P fertilizer treatments. All the treatments were replicated three times.

Eight seeds of PAN 4P-767BR maize (*Zea mays*) cultivar were planted per pot. After two weeks plants were thinned to four plants per pot. The amount of water applied as irrigation was based on pore volume calculations (Equation 5.5). Plants were watered daily to 75% of the pore volume. Water which drained through the pots was returned back to the soil surface, thus ensuring a closed drainage system. Pesticides and herbicides were not used during the experiment, and weeding was done by hand.

$$\Phi = 1 - (\boldsymbol{\rho}b/\boldsymbol{\rho}s) \quad \text{……. …….Equation 5.5}$$

Whereby: Φ= porosity (%), $\boldsymbol{\rho}b$ = bulk density (g cm^{-3}) and $\boldsymbol{\rho}s$ = particle density (taken to be 2.65 g cm^{-3}).

After six weeks growth, plant height and leaf area were measured; the latter using a leaf area meter Model (LI-3000). The plants were harvested at 1cm above soil level using pair of scissors, and dried at 70^{o}C to determine dry matter yield. Dried samples were ground and stored for plant nutrient analyses. Potting soil was air dried, and prepared for analysis by KZN Department of Agriculture and Environmental Affairs following procedures described by The non-Affiliated Soil Analysis Work Committee (1990)

5.2.2 Chemical analysis of plant tissue and soil

Oven-dried (70°C) samples were digested and analyzed for N, Ca, Mg, K, Na, Zn, Cu, Mn, Fe, P and Al by the procedure of Riekert and Bainbridge (1998) by the KZN Department of Agriculture, Fisheries and Forestry. Total P uptake (PU) was calculated from shoot dry matter and shoot P concentration. Soil from each pot was air dried, and prepared for analysis by the KZN Department of Agriculture, Fisheries and Forestry following methods given by The Non-Affiliated Soil Analysis Work Committee (1990). The soil samples were analyzed for extractable P, exchangeable K, Ca and Mg, exchangeable acidity, pH (KCl), and extractable Zn, Mn and Cu.

5.2.3 Statistical analysis

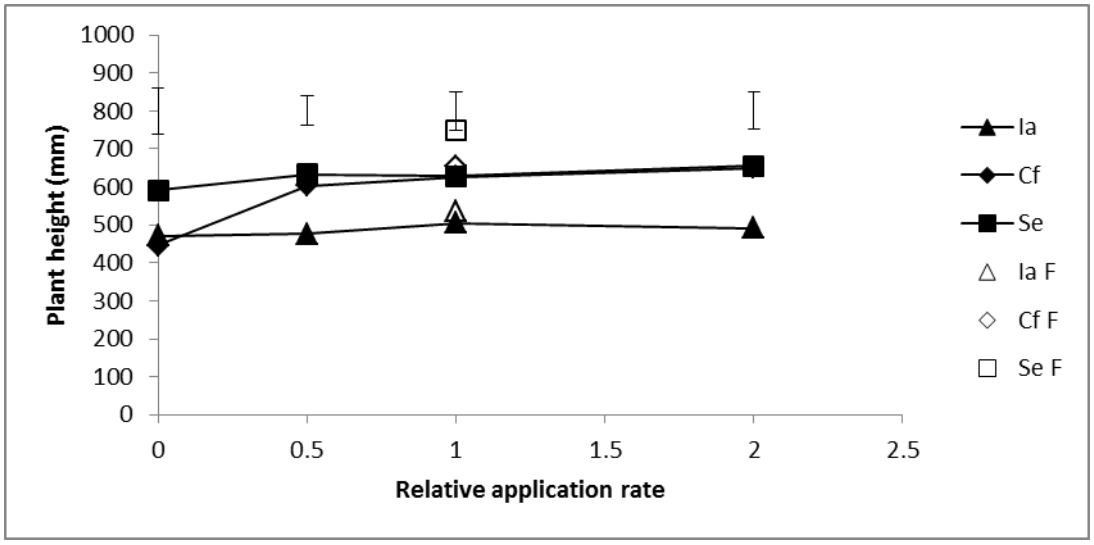
Statistical analysis was performed using Genstat statistical software (Version 12.1; 2009). Analysis of variance (ANOVA) was conducted by running a full model across soils. Mean separation was done using the least significant difference (LSD) at p=0.05. The effect of soil and P treatment (rate of struvite and SSP) and the interaction between these were evaluated.

5.3 Results

5.3.1 Effect of struvite application rate on maize plant height, leaf area and drymatter yield

The greatest response at half the recommended rate of struvite application, in terms of plant height, leaf area and dry-matter yield, was observed in the Cf followed by the Se and then the Ia, which did not respond to either struvite or SSP (Figure 5.1). For zero application rates (controls), the highest yield was recorded on the Se, which was the most inherently fertile of the soils used. The dry matter yield was almost constant for all soils and at all application rates beyond half the recommended rate (Figure 5.1), with the highest on the Cf and the least on the Ia. At the recommended rate there was no significant difference between struvite and SSP on both Cf and Ia (Appendix 5.2), whereas the SSP treatment was higher than struvite on the Se. The response to the SSP treatments was highest on the Se, and least response was recorded on the Ia.

(a)



(b)

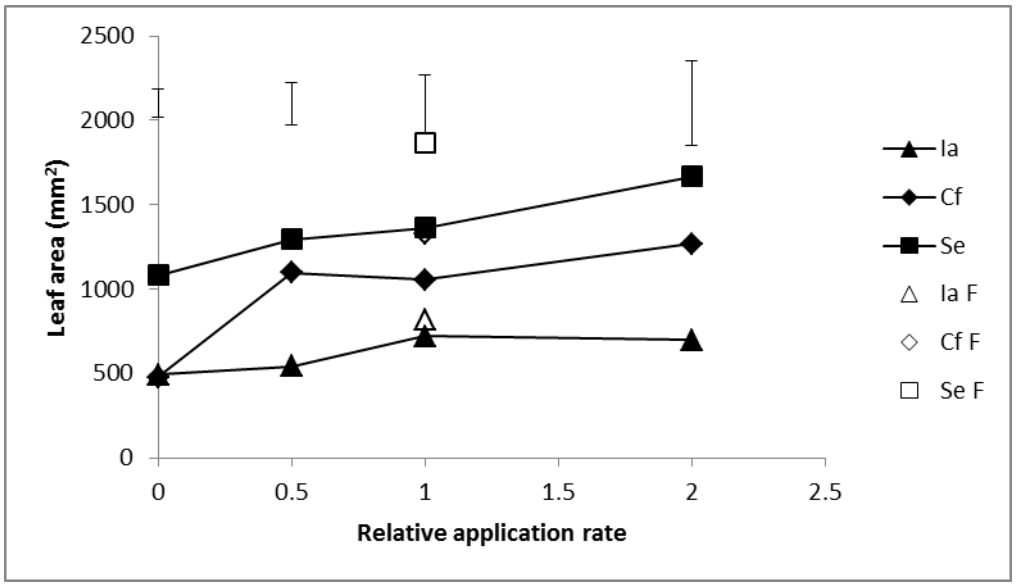
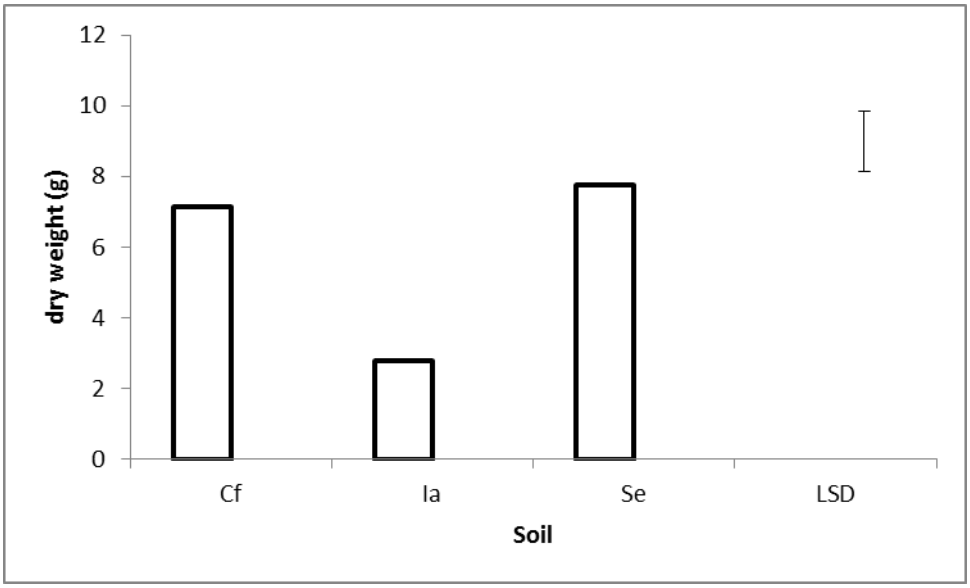


Figure 5.1(a&b): maize (a) plant height and (b) leaf area as a result of struvite application rates relative to the recommended phosphorus fertilizer rate on the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils. The unfilled symbols represent simple superphosphate (SSP) treatments for the corresponding soils. The error bars represents least significant differences (LSD at $p<0.05$).

(c)



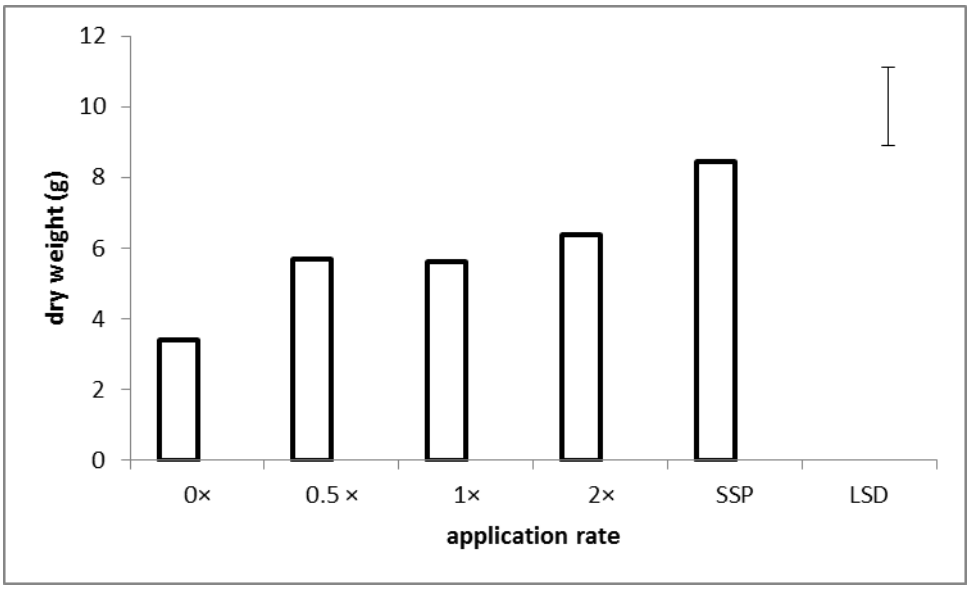


Figure 5.2 (c): maize dry matter yield response to struvite application rates relative to the recommended phosphorus fertilizer rate on the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils.. The error bars represents least significant differences (LSD at $p<0.05$).

5.3.2 Maize shoot phosphorus content as a function of different struvite application rates

In the Ia, there was no significant difference in P shoot content between the control and struvite treated pots (Figure 5.2). However, there was a small but non significant improvement in tissue P content in the SSP treated pots (Appendix and 5.2). At the recommended rate, struvite was not significantly different to SSP in terms of tissue P on the Cf, but twice the recommended rate of struvite treated plants had higher levels of P in the tissue than superphosphate treated plants . In this soil the tissue P increased with struvite application rate. Tissue P did not respond to struvite application rate or to SSP application in the Se (Figure 5.2). Maize grown on the Cf had the highest P content, followed by Se and Ia both for SSP and struvite. In contrast to the dry matter yield results, tissue P increased with application rate beyond half the recommended rate in the Cf, while SSP was similar to struvite at the recommended rate in Se.

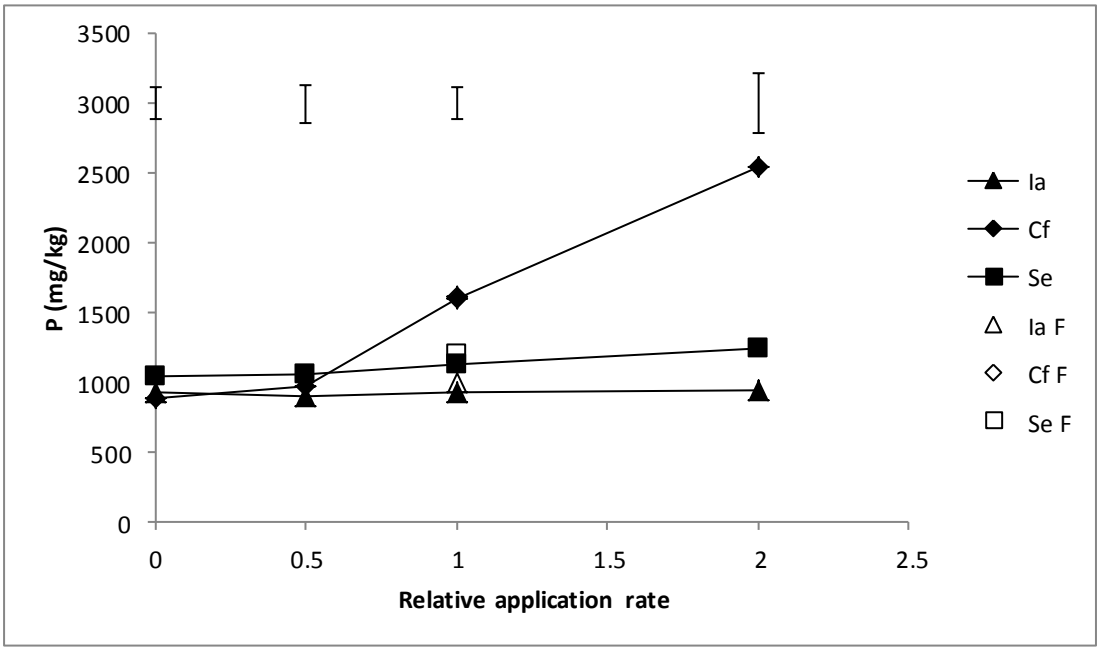


Figure 5.3 : Response of maize tissue phosphorus concentration to struvite application rates relative to the recommended phosphorus fertilizer rate on the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils. The unfilled symbols represent simple superphosphate (SSP) treatments for the corresponding soils. The error bars represents least significant differences (LSD at $p<0.05$).

The trends of P uptake in all the soils were similar to those of tissue P concentration except for the Se treated with SSP, which had higher uptake than a similar rate of struvite (Figure 5.3).

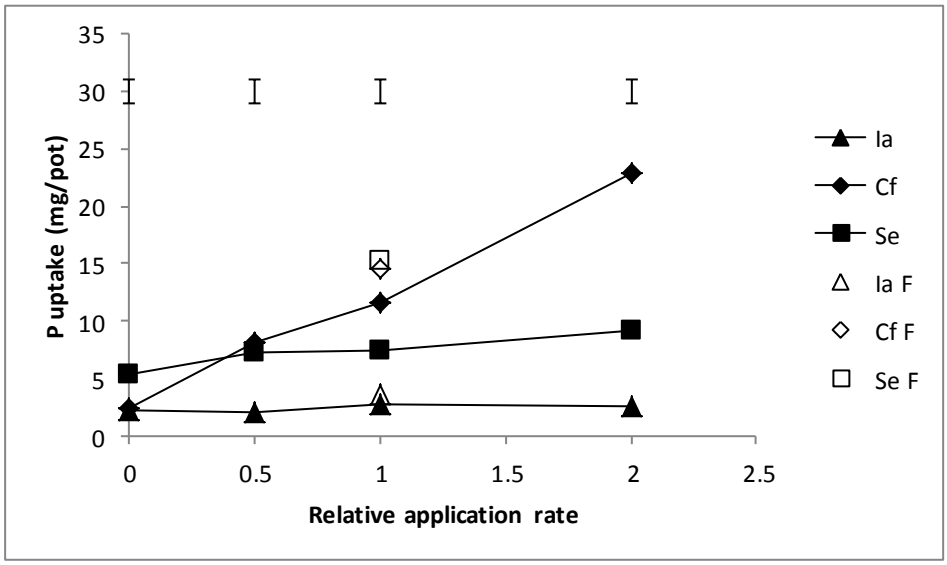


Figure 5.4: Response of maize phosphorus uptake to struvite application rates relative to the recommended phosphorus fertilizer rate on the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils. The unfilled symbols represent simple superphosphate (SSP) treatments for the corresponding soils. The error bars represents least significant differences (LSD at $p<0.05$).

5.3.3 Effect of struvite application rate on uptake of other nutrients

Uptake of other elements on the Ia and Se was higher in SSP treated pots compared to the struvite, except for Mn and Fe which were highest in the struvite treatment at the recommended rate in Ia (Table 5.1). On the Cf, uptake of N, K, Na, Zn, Cu and Fe were highest at half the recommended rate in the struvite treatment while Ca, Mg and Mn were highest in the SSP treatment. On the Se, uptake of all elements was highest in the SSP treatment. The uptake of N in the Se was almost two times higher than that of Ia and Cf (Table 5.1). The uptake of Ca, Mg, K, and micronutrients was lower in the Ia than the other two soils.

5.3.4 Effect of struvite on soil solution P content at harvest

At harvest the Ia had the highest amount of extractable P followed by the Cf and Se, respectively (Figure 5.4). When struvite was applied at half the recommended rate the soil solution P in the Se was similar to that of the Cf, and the trend was similar to that of P uptake (Figure 5.3). On the

Se, half and twice the recommended rate had higher extractable soil P content compared to the recommended rate. The P concentration in the SSP treated Ia soil was lower than in the struvite treated soil at equal application rates (Figure 5.4). On the Cf, SSP treated pots had similar P in solution compared to struvite treated pots. On the Se, SSP treated pots had higher P content compared to struvite.

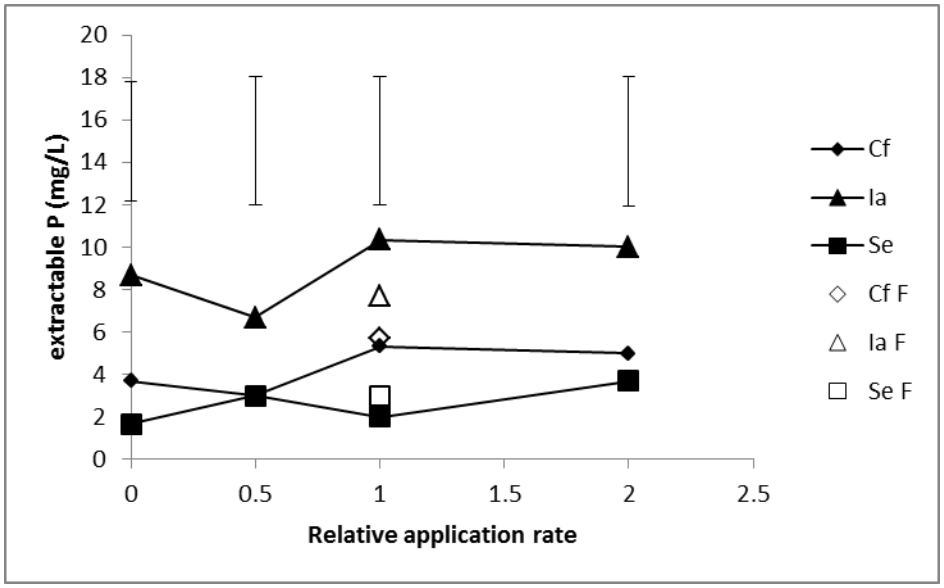


Figure 5.5: Extractable phosphorus concentration (mg L^{-1}) in the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils after harvest of maize as affected by struvite application rate. The unfilled symbols represent SSP treatments for the corresponding soils. The error bars represents least significant difference (at $p < 0.05$).

5.3.5 Effect of struvite application rate on soil nutrient composition at harvest

The concentration of all elements in the soil at harvest were in the order; Se>Ia>Cf. The concentration of Ca, Mg, Zn, Mn and Cu, were highest in the SSP treatment, K was highest in the twice the recommended rate struvite treatment for the Ia. In the Se, Mg and K were highest in the control; Zn and Cu were highest in the struvite treatment at the recommended rate while Ca and Mn were highest in SSP. In the Cf, K and Mn were highest in the SSP while Ca and Mg were highest in the struvite treatment at twice the recommended rate (Table 5.2).

Table 5.1: Uptake of elements (mg pot^{-1}) by maize fertilized with struvite as affected by struvite application rate relative to single superphosphate (SSP) in the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils

	Ia					Cf					Se					LSD
	Control	Struvite			SSP	Control	Struvite			SSP	Control	Struvite			SSP	
Element (mg pot^{-1})		0.5×	1×	2×			0.5×	1×	2×			0.5×	1×	2×		
N	4.42	7.05	8.02	8.87	9.02	3.25	7.58	6.85	8.34	8.74	10.04	15.55	16.08	20.74	25.19	5.92
Ca	0.91	0.93	1.15	1.06	1.73	1.16	3.00	2.70	3.37	3.53	1.49	2.90	3.22	2.81	5.15	1.85
Mg	1.24	1.19	1.09	1.36	2.30	1.53	3.50	2.92	3.76	3.53	2.03	4.37	5.46	3.68	6.47	2.89
K	6.14	8.04	8.78	8.46	8.21	5.48	26.04	8.92	15.06	19.13	13.33	19.67	17.99	23.46	36.56	7.45
Na	0.35	0.43	0.64	0.58	0.74	0.41	1.77	0.85	1.35	1.18	0.90	1.73	1.12	1.42	2.73	0.75
Zn	0.06	0.09	0.10	0.10	0.11	0.06	0.33	0.11	0.17	0.25	0.14	0.23	0.23	0.25	0.35	0.01
Cu	0.01	0.01	0.01	0.01	0.02	0.01	0.04	0.02	0.04	0.03	0.02	0.03	0.03	0.03	0.07	0.02
Mn	0.39	0.69	0.92	0.77	0.77	0.36	2.14	1.32	1.37	2.47	0.82	1.08	0.28	1.81	2.73	0.84
Fe	0.16	0.22	0.42	0.27	0.31	0.17	0.83	0.40	0.49	0.71	0.35	0.62	0.56	1.42	1.21	0.70

Table 5.2: Concentration of various elements and pH after the pot trial harvest of maize as affected by struvite application rate relative to single superphosphate (SSP) in the Inanda (Ia), Cartref (Cf) and Sepane (Se) soils

	Ia					Se					Cf					LSD
parameter		Struvite					struvite					struvite				
	Control	0.5 ×	×1	2×	SSP	Control	0.5×	1×	2×	SSP	Control	0.5×	×1	×2	SSP	
Mg (mg L^{-1})	17	20.3	17.7	21.7	52.3	964.7	935	901	866.7	921	69.3	55.3	64.7	79	54.7	92
Ca (mg L^{-1})	73	70	58	69	166	1750	1759	1753	1732	1765	296	325	363	299	304	167
K(mg L-1)	39	58	55.3	64.3	55.7	79.3	67.3	77.3	75.3	76.7	13.7	15.3	13.7	21.3	15.3	20
Exchangeable acidity (cmol L^{-1})	2.02	2.47	2.56	2.69	2.23	0.05	0.07	0.06	0.08	0.21	0.06	0.09	0.08	0.08	0.073	0.2
pH (KCl)	3.89	3.90	4.32	4.56	4.62	5.707	5.61	5.68	5.64	5.71	4.66	4.68	4.53	4.61	4.45	0.1
Zn (mg L^{-1})	2.8	3.05	1.1	2.45	4.05	1.4	4.2	4.6	0.85	0.75	2.85	1.05	0.667	1.27	1.2	0.9
Mn (mg L^{-1})	21	12.5	8	13.5	16.33	15	20.5	22	10	24	24	15	18.67	18	26.5	10
Cu (mg L^{-1})	2.36	1.05	1.93	2.95	3.1	3.4	3.6	3.85	1.8	1.75	2.7	1.85	1.5	1.95	1.5	0.9

5.4 Discussion

The results suggest that struvite can be as effective as superphosphate except in the Se where single superphosphate gave a significantly higher yield compared to struvite. Antonini et al. (2012) considered water solubility to be the primary driving factor of struvite effectiveness and it is likely that low struvite solubility in the high pH Se limited the response.

The minimal plant height, leaf area and dry matter yield response to both P fertilizers in the Ia (Figure 5.1) could be explained by the high exchangeable acidity. Gichangi et al. (2008) reported that P availability has a strong negative correlation with exchangeable Al, possibly due to precipitation of Al-phosphates. However, higher extractable P in the Ia than both the Cf and Se suggests that the limited yield response in this soil was not due to unavailability of P. Since the soils were not limed, Al toxicity might have affected uptake of nutrients and thus yield in the strongly acidic Ia (Chen, 2006). This is supported by the low uptake of Ca, Mg, K, and micronutrients in this soil at all struvite rates and SSP compared to the other two soils. This would have been worsened by the low natural fertility of the Ia (Table 3.1). The lack of yield response and P uptake to struvite application in the Se is in agreement with Massey et al. (2009) on neutral to alkaline soils. This is probably a result of minimal dissolution of struvite in this soil that had a pH of 7 thus resulting in low P availability to the plants. This was supported by the soil extractable P concentration at the end of the experiment which was higher in the SSP treated soil than that treated with struvite. Although the Se had the highest uptake of all other elements measured, yield was limited due to a lower P uptake than the Cf.

The high plant height, leaf area, dry matter yield and shoot P uptake on the Cf soil was due to availability of P and other nutrients at pH 6. This is in agreement with Massey et al. (2009) on soils of similar pH. They also observed that soils with high pH limit struvite solubility and hence plant nutrient uptake. At the pH of the Cf soil, struvite could have dissolved sufficiently and in this sandy soil the P would have been easily available to the maize. Based on the results of this study, it is evident that the effectiveness of struvite as a P source is dependent on its properties and those of the soil involved. Solubility of struvite as affected by soil pH seems to be a major determining factor with regards to struvite effectiveness as a P fertilizer. This is supported by the maize P uptake results (Figure 5.3) that showed that with SSP the Se gave higher P uptake than the Cf, whereas with struvite the Cf had higher P uptake than the Se. Since superphosphate is

readily soluble P was not limited in Se whereas struvite solubility is pH dependent and thus the high pH of the Se will have limited the solubility of struvite. It is also possible that Ca or Mg phosphates could have formed in the soil, given the high base status of Se and high pH values, and these are much less soluble given the pH of the local environment as shown in Chapter 3. So although the struvite might have dissolved, the P was unavailable to the plants.

The soil P concentration after the experiment in the Ia was higher on struvite treated pots than SSP treated pots. These results are similar to some of the findings which have been made on PR by He et al. (2005), whereby PR can be more effective than SSP under certain conditions. The higher concentration of all other measured elements in the Se could be explained by the higher initial fertility of this soil, while concentrations were intermediate in the Ia because of poor initial fertility coupled with low uptake due to poor plant growth. In the Cf, greater dry matter accumulation resulted in greater uptake leaving the soil with lower concentrations of the measured elements (Table 5.2).

5.5 Conclusions

The effectiveness of struvite as a P fertilizer varies from soil to soil due to differences in solubility and sorption properties of the soils. Struvite is most effective in supplying P in soil of moderate or low pH but is much more limited in high pH soils. Even though struvite is more soluble in acidic soils its effectiveness could be limited by poor natural fertility and high Al toxicity and P sorption. Struvite application above half the recommended rate did not increase dry matter yield in a short-term glasshouse study, although these effects could be evident if the study was carried out over the whole maize growing season. The positive effects of struvite in the sandy soil (Cf) need to be tested under field conditions where leaching will occur. Nonetheless, the results conclusively suggest that struvite has great potential as a phosphorus source for growing maize.

CHAPTER 6

GENERAL DISCUSSION, CONCLUSIONS AND FUTURE WORK

6.1 Introduction

There is potentially a threat to the future supply of phosphorus and the cost of phosphate fertilizer over the last decade has increased sevenfold. Human urine is a ubiquitous "resource" which can be used as a source of phosphorus. The sanitation systems of many developing countries require improvement and this will enable human urine to be separated at source and then considered as a possible P source for subsistence and commercial farmers, hence improving food security.

The use of human urine has a number of logistical problems and most of these can be overcome by converting urine into the solid material, struvite, by the addition of magnesium. The incongruent (and low) dissolution property of struvite makes it a notably different material when compared with the easily soluble commercial phosphate fertilizers. However, there have been no studies in South Africa on the potential of struvite as an alternative phosphate fertilizer for crops. The main objectives of this study were thus to investigate the P and Mg release behaviour of struvite in three South African soils and to evaluate its potential as a P fertilizer for maize in the same soils.

6.2 Agricultural implications of struvite as an alternative P source

Through sorption studies it was established that the three contrasting soils used varied greatly in their ability to retain and release P. The Ia had the highest sorption followed by the Se and Cf, respectively. From these initial sorption data, the solubility product principle was applied and it was concluded that in the Ia struvite will solubilize readily, followed by the Se and Cf, respectively. The incubation results, showed that P was indeed highest in the Ia and that the nutrient release rate was also the highest in this soil. However, in the Se, it appears that pH is a much stronger variable and was controlling struvite solubility. Massey et al. (2009) found that

struvite solubility is inversely proportional to pH and this applied to the three soils used here with dissolution following the trend Ia > Cf > Se while soil pH followed the opposite trend.

The incubation results provided evidence that struvite can solubilize and release P with the extent of dissolution being inversely proportional to the pH of the soil. To test the effectiveness of this released P on P uptake by plants a pot experiment was conducted using maize (*Zea mays*) as the test crop. In the three soils the extractable soil P at harvest was different for the struvite treated pots compared to the SSP treatments. In the Ia the amount of soil P in struvite treated pots was greater than in SSP treated pots; in the Cf the soil P contents were equal in all treatments; and in the Se the soil P content at harvest in struvite treatments was less than that where SSP had been applied.

However, the plant analysis results were less dependent on extractable P except in the Cf, where there was a close correlation with P uptake. The inherent high fertility of the Se enabled it to have higher dry matter yields and nutrient uptake on the struvite treated pots than the Ia, which had low inherent fertility. Of all the treatments and among all the soils, the highest dry matter yield was in the Se treated with SSP, and this could be explained by the combination of high inherent fertility and unlimited dissolution of SSP compared to struvite (Massey et al., 2009). In the struvite treatments the lower yield in the Se compared to Cf could be explained by the low dissolution of struvite in the Se with pH 7.1 than the Cf with pH 6.3. In addition, P sorption in the Cf was low, due to the sandy texture, making P more available with no leaching in a non-draining environment, resulting in greater response. Dissolution of struvite decreases with an increase in pH (Massey et al., 2009). Although the Ia had the highest extractable P it had the lowest dry matter yield and P uptake. This could be explained by low total bases in combination with high exchangeable acidity, which could have resulted in Al toxicity affecting uptake of all other nutrients. This is supported by the lower uptake of Ca, Mg and K and micronutrients by the maize, than on the Se and Cf. Although the results of soil pH in the incubation study and after harvest of the glasshouse experiment show that struvite has a liming effect, this effect was not large enough to reduce the exchangeable acidity in the Ia to acceptable levels for maize growth. However, this liming effect could be more effective with repeated use of struvite in this soil or in other soils with lower acidity than the Ia used in this study. The uptake of Zn, Cu, Mn, Ca and K was highest in the Cf while the Ia had the lowest uptake of macro and micronutrients. This further perhaps suggests that other growth limiting factors which are less related to the plant

nutrient uptake were dominant as results indicated that the concentration of these nutrients in the soil was highest in the Ia compared to Cf except for the Ca and Mg.

These results illustrate the importance and potential benefits of using a slow release fertilizer on soils with a high P sorption capacity. If applied to soils with high sorption capacity, such as the acidic Ia, struvite can continuously supply P in a more available form, compared to a readily soluble superphosphate which supplies P rapidly but much of which is equally rapidly adsorbed and is thus unavailable to plants. This may explain in the Ia the high amount of extractable soil P in the struvite treated pots at harvest compared to SSP treated pots. The results of the Cf adsorption studies confirm, as expected from the soil texture, that the Cf has a low P sorption capacity. The incubation studies suggest that P in the Cf is controlled mainly by dissolution/precipitation reactions rather than adsorption/desorption reactions, and its pH was not limiting for struvite dissolution. These factors perhaps explain the equality in soil P between struvite and SSP treated pots at harvest. In the Se the soil P content was a function of the poor dissolution of the struvite in this higher pH soil.

6.3 Recommendations for the future work

The current work has shown that struvite can potentially be used in some soils and can be comparable to commercial superphosphate. However, there are some major gaps which still need to be filled regarding the use of struvite. There is a large body of literature on the behaviour of phosphorus in soils and this forms the background to the possible reactions P released from struvite might undergo. However, it is likely that the dissolution of struvite has more in common with that of phosphate rock than commercial superphosphates. The self-liming effect of struvite in the strongly acid soil and the lack of response on the high pH soil found in this work are examples of this comparison. It is thus likely that more work similar to that carried out in the current study but using different types of phosphate rock (reactive and less reactive) as comparative fertilizers could be worthwhile. Another aspect of struvite solubility not studied here is the effect of different particle size fractions since it is likely that the finer the particle size the faster and more complete dissolution will be, perhaps even under less than ideal circumstances. Also, if the comparison with PR is continued then it might be possible to either

partially acidulate struvite to make it more soluble or to supply a coating that enhances its dissolution.

It is also recommended that future studies must be conducted so as to understand fully the effect of struvite through field experiments with a variety of crops. The effect of struvite on soil physical properties (with a focus on the presence of sodium) and nutrient dynamics needs further investigation so as to understand fully the potential, limitations and any possible drawbacks from using struvite. The effects of soil pH on struvite solubility and the self-liming ability of struvite need to be researched more fully with some emphasis given to the 'local', i.e. close to the dissolving struvite granule, effect that a high pH may have on the soil particles and the products formed. The comparison between the extremely low pH that develops close to a superphosphate granule in soil and the high pH when struvite dissolves and their respective effects on adjacent soil particles requires further investigation. Despite these significant gaps in research with regards the agricultural use of struvite, the current work has clearly shown that it has considerable potential as an alternative P source and has indicated the soil conditions under which such potential will be realised. The challenge remains to extend these conditions to soils with apparently less than ideal properties to do so under a variety of field conditions in South Africa. If this can be achieved then struvite could well become an economic alternative to current commercial superphosphates and thus assist in mitigating any future threat to their supply. It is also essential to evaluate and model the logistics regarding struvite production, and evaluate what is the potential for this innovation to be for adopted in South Africa.

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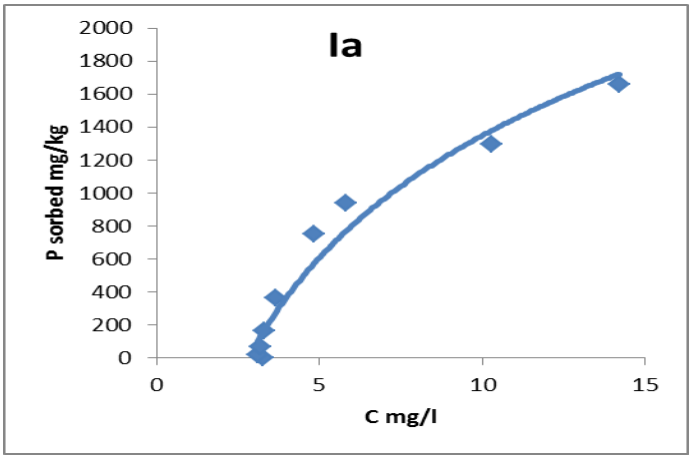
APPENDICES

Appendix 3.1: EC of NH_4OH at various percentages

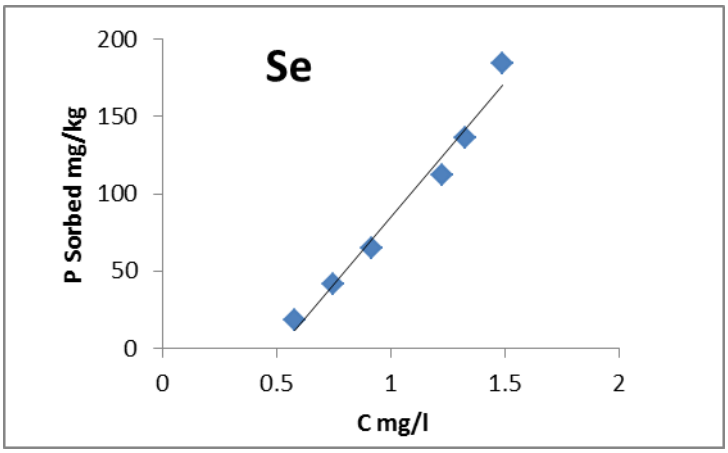
% of NH_4OH	EC ($\mu S\ cm^{-1}$)
0.01	9.29
0.1	10.42
1	11.03
5	32.06

Appendix 4.1: Phosphorus sorption isotherms

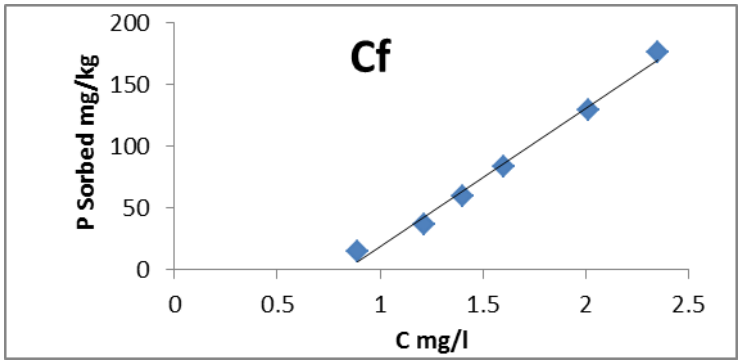
(a)



(b)



(c)



Appendix 4.2: Changes in concentration of exchangeable bases (mg L^{-1}) in the Inanda (Ia) during the second incubation

Mg

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	2	4	8	16	22
control	0.47	0.52	0.56	0.61	0.38	0.65
0.035	0.61	0.61	0.61	0.70	0.70	0.70
0.11	0.76	0.66	0.68	0.68	0.73	0.86
0.175	0.66	0.76	0.78	0.92	0.80	1.21

K

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	2	4	8	16	22
control	1.35	1.13	1.32	2.59	2.31	2.45
0.035	1.16	1.38	1.17	2.45	1.92	2.59
0.11	1.26	1.24	1.35	2.63	2.02	2.74
0.175	1.39	1.18	1.05	2.30	1.97	3.03

Ca

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	2	4	8	16	22
control	2.24	2.42	2.36	3.25	2.83	3.08
0.035	2.08	2.66	2.42	3.11	2.23	3.49
0.11	2.29	2.39	2.74	2.89	2.59	3.97
0.175	2.47	2.32	1.98	2.84	2.19	3.53

Na

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	2	4	8	16	22
control	1.38	1.39	1.59	1.73	1.45	1.52
0.035	1.52	1.59	1.34	1.45	1.48	2.00
0.11	1.53	1.54	1.38	1.47	1.42	1.94
0.175	1.77	1.57	1.49	1.54	1.48	1.80

Appendix 4.3: Changes in concentration of exchangeable bases (mg L^{-1}) in the Sepane (Se) during second incubation

Mg

Application rate (g struvite kg^{-1} soil)	**Time (days)**					
	1	**2**	**4**	**8**	**16**	**22**
control	31.89	22.13	22.11	22.81	29.55	30.69
0.065 (g struvite/ kg)	23.13	26.67	26.14	26.13	30.42	31.84
0.2 (g struvite/kg)	31.77	27.71	26.98	28.75	32.70	32.78
0.4 (g struvite/kg)	30.83	31.74	30.80	34.19	33.41	35.48

K

Application rate (g struvite kg^{-1} soil)	**Time (days)**					
	1	**2**	**4**	**8**	**16**	**22**
control	4.58	3.15	2.72	3.58	3.74	3.96
0.065	3.20	4.41	4.04	4.03	3.96	4.18
0.20	3.50	4.55	3.83	3.64	4.05	4.19
0.39	4.00	5.17	4.45	4.41	4.02	3.48

Ca

Application rate (g struvite kg^{-1} soil)	**Time (days)**					
	1	**2**	**4**	**8**	**16**	**22**
control	54.22	45.51	37.47	44.03	57.53	48.46
0.065	55.43	54.24	55.64	56.02	60.66	61.01
0.20	50.03	49.21	50.14	47.10	56.63	49.27
0.39	56.04	60.14	55.46	57.85	59.03	65.48

Na

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	2	4	8	16	22
control	6.57	3.81	4.16	4.79	6.69	6.68
0.065	6.44	5.77	5.73	5.69	6.48	7.09
0.2	5.77	4.87	5.21	4.31	6.83	7.39
0.39	6.23	6.69	5.92	5.71	7.09	6.69

Appendix 4.4: Changes in concentration of exchangeable bases (mg L^{-1}) in the Cartref (Cf) during second incubation (a) Mg (b) K (C) Ca (d) Na

Mg

Application rate (g struvite kg^{-1} soil)	**Time (days)**					
	1	**2**	**4**	**8**	**16**	**22**
Control	1.90	1.88	1.99	1.77	1.72	2.09
0.07	2.07	2.14	2.13	2.02	1.44	2.74
0.21	2.24	2.26	2.14	2.15	2.05	2.95
0.42	2.50	2.61	2.65	2.57	2.77	3.08

K

Application rate (g struvite kg^{-1} soil)	**Time (days)**					
	1	**2**	**4**	**8**	**16**	**22**
Control	1.28	1.36	1.70	0.81	0.56	1.38
0.07	1.32	1.30	1.44	0.51	1.46	0.68
0.21	1.37	1.25	1.56	0.48	1.30	0.43
0.42	1.57	1.52	1.62	0.53	1.65	1.14

Ca

	Time (days)					
Struvite application rate (g struvite kg^{-1} soil)	**1**	**2**	**4**	**8**	**16**	**22**
Control	2.46	4.54	4.61	6.07	3.77	3.78
0.07	2.68	6.20	6.98	7.37	4.02	7.25
0.21	4.79	7.61	5.71	7.11	4.35	6.14
0.42	4.61	8.30	8.07	8.00	9.89	9.59

Na

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	**2**	**4**	**8**	**16**	**22**
Control	1.91	1.73	1.76	1.97	1.96	2.24
0.07	1.54	1.79	1.71	2.12	2.02	2.21
0.21	1.53	1.74	1.71	1.99	2.02	2.52
0.42	1.60	2.12	1.78	2.14	2.43	2.40

Appendix 4.5: Calcium to magnesium ratio changes during second incubation

Ia

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	**2**	**4**	**8**	**16**	**22**
control	4.77	4.62	4.18	5.36	7.40	4.70
0.035	3.43	4.34	3.9	4.45	3.19	5.01
0.11	2.99	3.63	4.00	4.22	3.53	4.62
0.175	3.74	3.05	2.53	3.09	2.72	2.91

Se

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	**2**	**4**	**8**	**16**	**22**
control	1.70	2.05	1.69	1.92	1.94	1.57
0.065	2.39	2.03	2.12	2.14	1.99	1.91
0.20	1.57	1.77	1.85	1.63	1.73	1.50
0.39	1.81	1.89	1.80	1.69	1.76	1.84

Cf

Application rate (g struvite kg^{-1} soil)	Time (days)					
	1	**2**	**4**	**8**	**16**	**22**
Control	1.29	2.41	2.31	3.43	2.19	1.80
0.07	1.29	2.90	3.28	3.65	2.79	2.64
0.21	2.13	3.36	2.66	3.31	2.11	2.08
0.42	1.84	3.17	3.05	3.11	3.57	3.10

Appendix 4.6: Changes in pH in water (H_2O) and potassium chloride (KCl) during the first incubation

Ia	H_2O								KCl							
	Time (days)															
Application rate (g struvite kg^{-1} soil	**1**	**2**	**4**	**8**	**16**	**28**	**64**	**128**	**1**	**2**	**4**	**8**	**16**	**28**	**64**	**128**
0.035	4.86	5.11	4.88	4.02	3.96	3.93	4.25	3.85	3.73	3.93	3.83	4.21	4.18	4.14	4.29	4.17
0.07	4.88	4.82	4.88	3.86	3.95	3.9	4.3	3.7	3.73	3.95	3.94	4.19	4.19	4.17	4	4.18
0.1	4.86	4.87	4.82	3.9	4.12	3.85	4.24	4.06	3.72	3.96	3.96	4.19	4.20	4.19	4.02	4.19
0.14	4.87	4.86	4.86	3.9	3.92	3.84	4.2	3.83	3.73	3.94	3.98	4.2	4.18	4.21	4.03	4.2
0.17	4.88	4.86	4.84	3.84	3.96	3.77	4.21	3.78	3.74	3.96	3.97	4.19	4.17	4.19	4.04	4.2
0.2	4.85	4.92	4.86	4.03	3.92	3.82	4.12	3.8	3.72	3.96	3.97	4.2	4.19	4.16	4.01	4.19

Se	H_2O								KCl							
	Time (days)															
Application rate (g struvite kg^{-1} soil)	**1**	**2**	**4**	**8**	**16**	**28**	**64**	**128**	**1**	**2**	**4**	**8**	**16**	**28**	**64**	**128**
0.065	7.35	7.08	7.12	6.12	6.19	6.16	7.3	6.52	5.79	5.78	5.79	5.95	6.03	5.96	5.93	5.94
0.1	7.39	7.13	7.23	6.17	6.16	6.11	7.15	6.43	5.93	5.86	5.86	5.98	5.98	6.01	6	5.97
0.2	7.46	7.19	7.12	5.97	6.04	6.16	7.18	6.44	5.88	5.89	5.85	5.91	6.00	5.94	6.06	5.9
0.26	7.37	7.21	7.49	6.32	6.44	6.79	7.73	7.17	5.9	5.9	5.93	6.16	6.22	6.42	6.32	5.9
0.3	7.39	7.33	7.43	6.19	6.31	6.54	7.55	6.56	5.81	5.94	5.96	6.1	6.12	6.24	6.28	6.38
0.4	7.36	7.32	7.26	6.06	6.37	6.34	7.3	6.5	5.94	5.93	6	6	6.17	6.11	6.15	6.15

Cf	H_2O								KCl							
Application rate (g struvite kg^{-1} soil)	**Time (days)**															
	1	**2**	**4**	**8**	**16**	**28**	**64**	**128**	**1**	**2**	**4**	**8**	**16**	**28**	**64**	**128**
0.07	7.28	6.78	6.77	5.22	5.46	5.30	6.71	5.37	6.08	5.41	5.53	5.71	5.72	5.36	5.45	6.01
0.14	6.77	6.74	6.72	5.4	5.39	5.30	6.4	5.49	5.43	5.6	5.62	5.76	5.6	5.47	5.27	5.25
0.21	7.07	6.86	6.89	5.44	5.51	5.65	6.36	5.28	5.67	5.82	5.74	5.8	5.74	5.55	5.35	5.26
0.28	7.15	7.03	7.14	5.68	5.66	5.54	6.52	5.31	6	5.7	5.98	5.99	5.97	5.58	5.62	5.36
0.35	6.92	6.81	7.16	5.81	5.87	5.63	6.44	2.61	5.6	5.68	6.1	5.92	6.21	5.61	5.53	5.27
0.42)	6.64	7.11	7.18	5.86	5.51	4.86	5.71	3.53	5.25	5.84	6.06	5.98	5.73	5.27	5.09	4.91

Appendix 4.7: Changes in pH in water (H_2O) and potassium chloride (KCl) during the second incubation

Ia	H_2O						KCl					
Application rate (g struvite kg^{-1} soil)	**Time(days)**											
	1	**2**	**4**	**8**	**16**	**22**	**1**	**2**	**4**	**8**	**16**	**22**
Control	4.80	4.92	4.92	4.84	4.85	4.74	3.94	3.95	3.93	3.94	3.96	3.95
0.035	4.91	4.90	4.97	4.91	4.83	4.74	3.94	3.92	3.93	3.94	3.97	3.96
0.1	4.90	4.94	4.94	4.83	4.81	4.75	3.95	3.94	3.94	3.95	3.96	3.96
0.17	4.93	4.96	4.99	4.87	4.85	4.77	3.94	3.92	3.94	3.94	3.97	3.97

Se	H_2O						KCl					
	Time (days)											
Application rate (g struvite kg^{-1} soil)	**1**	**2**	**4**	**8**	**16**	**22**	**1**	**2**	**4**	**8**	**16**	**22**
Control	7.32	7.40	7.39	7.21	6.85	6.68	6.02	6.03	6.02	5.97	5.89	4.95
0.065	7.39	7.38	7.37	7.24	6.79	6.69	6.05	6.07	6.03	6.01	5.92	4.95
0.26	7.39	7.45	7.39	7.20	6.86	6.79	6.08	6.15	6.08	6.05	5.94	5.11
0.4	7.35	7.44	7.44	7.13	6.80	6.66	6.09	6.08	6.06	6.01	5.87	5.07

Cf	H_2O						KCl					
	Time (days)											
Application rate (g struvite kg^{-1} soil)	**1**	**2**	**4**	**8**	**16**	**22**	**1**	**2**	**4**	**8**	**16**	**22**
control	6.31	6.50	6.45	6.54	6.53	6.25	6.02	6.03	6.02	5.90	5.97	5.72
0.07	6.49	6.56	6.48	6.52	6.53	6.32	6.05	6.07	6.03	5.92	6.01	5.77
0.21	6.58	6.64	6.59	6.72	6.54	6.52	6.08	6.15	6.08	5.94	6.05	5.77
0.42	7.02	6.69	6.80	6.59	6.63	6.22	6.09	6.08	6.06	5.87	6.01	5.75

Appendix 5.1: Analysis of variance for (a) shoot dry matter (b) P content in the tissue (mg kg^{-1}) and (c) P uptake (PU) (mg pot^{-1}) after six weeks growth of maize with four different rates of struvite and the recommended rate of single superphosphate in three contrasting soils in a glasshouse experiment

(a)

Variate: shoot_dry

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Soil	2	221.346	110.673	21.23	<.001
Treatment	4	117.910	29.477	5.66	0.002
Soil.Treatment	8	68.914	8.614	1.65	0.152
Residual	30	156.360	5.212		
Total	44	564.530			

(b)

Variate: P_mg_kg

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Soil	2	2651724.	1325862.	59.87	<.001
Treatment	4	2288312.	572078.	25.83	<.001
Soil.Treatment	8	3108510.	388564.	17.55	<.001
Residual	30	664342.	22145.		
Total	44	8712889.			

(c)

Variate: PU

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Soil	2	6.523E+08	3.261E+08	26.27	<.001
Treatment	4	4.685E+08	1.171E+08	9.43	<.001
Soil.Treatment	8	4.538E+08	5.672E+07	4.57	0.001
Residual	30	3.725E+08	1.242E+07		
Total	44	1.947E+09			